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Sampling and Analysis of Reduced and Oxidized Species in Process Streams

TRW Defense and Space Systems Group
Redondo Beach, CA

Prepared for

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16. ABSTRACT

The report gives results of a program of over 60 tasks involving the evaluation, development, testing, and field adaptation of measurement techniques for elemental analysis and inorganic compound identification in process and effluent streams. Procedures for particulate sampling at the inlet and outlet of FGD systems were developed. Methods for H2SO4 sampling in flue gas streams were developed based on the controlled condensation of H2SO4 vapor (a manual procedure was used as the basis for an automated H2SO4 monitoring instrument that was built and tested). Two procedure manuals were written for reduced and oxidized inorganic species. The reduced species manual detailed GC and GC/MS procedures for identifying organometallic compounds as well as homologous series such as RSH and RNH. The oxidized species were identified using an integrated series of analytical methods such as AAS, ICAP, XRD, FTIR, ESCA, and SEM-EDX. The procedures developed, applied to samples from several EPA programs, showed that the analysis scheme is applicable to most solid samples from combustion sources. Ion chromatographic procedures were also developed for analyzing FGD system slurry streams. The use of pH and chloride electrodes for controlling FGD systems was investigated. The methodology for coal flow monitors was reviewed.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Oxidation	Pollution Control	13B	
Sampling	Industrial Processes	Stationary Sources	14B	13H
Analyzing	Dust	Particulate		11G
Measurement	Aerosols			07D
Inorganic Compounds			07B	
Reduction (Chemistry)				
Sulfuric Acid				

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by

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INTRODUCTION

This program (EPA Contract No. 68-02-2165) was sponsored by the Process Measurements Branch of the Industrial Environmental Research laboratory at Research Triangle Park, North Carolina. The original program officer was Dr. Robert Statnick, and the current program officer is Mr. Frank Briden. Under this contract, TRW conducted a program for the evaluation, development, testing and field adaptation of measurement techniques for elemental analysis and inorganic compounds identification in process and effluent streams. The primary objective of this program was to provide the measurement methodologies required for environmental assessment and control technology development projects related to the stationary source, energy and industrial process programs of the EPA. TRW was responsible for conducting both the basic development effort and the programs necessary to apply and evaluate the application of these and other sampling and analytical techniques on specific engineering studies.

Many of the tasks initiated covered short-lived or routine activities and were not reported. The tasks covered in this final report represent the technical work performed under this program. This report contains an executive summary which describes the entire program in each of the individual areas defined in the program scope of work. Following this summary are detailed reports on each of the key tasks in the program. Descriptions and objectives of each task are discussed followed by the technical approach, techniques used, and results applicable to each task. Appropriate recommendations and comments are included at the end of each task discussion. In addition to a discussion of major tasks, a brief synopsis of <100 hour tasks follows the major tasks. A compilation of reports issued by task on the program are found in Section 4.

SECTION 1
EXECUTIVE SUMMARY

The work performed on this contract can be divided into six major work areas:

1. Measurement Methods Evaluation and Development
2. Methods Adaptation and Application Studies
3. Measurement and Test Program Reviews
4. Sampling and Analytical Support
5. Preparation of Guidelines and Procedures
6. Conduct Symposia and Training Sessions.

It was the original intent of the program to direct the bulk of the work into R&D activities. Based on areas 1 and 2 TRW spent approximately 66% of the hours in pursuit of new methods or on the evaluation and adaptation of available methodology.

Program work areas are shown in Table 1 along with the tasks performed and percentage of the hours expended for each area. Of particular note are tasks 7, 8, 10, 13, 47, 48 and 62 in the Measurement Methods Evaluation and Development area. These tasks dealt with state of the art environmental sampling and analysis methods for oxidized (Task 7) and reduced (Task 8) inorganic species; coal sulfur measurements (Task 10); SO_3 measurements (Tasks 13 and 47); ion chromatography (Task 48); and process measurement of pH and Cl^- (Task 62). The following pages will summarize the tasks performed in each of the six work areas.

TABLE 1. TLE TASK EXPENDITURES BY AREA

Area	Tasks	% of Total Expenditures
1. Measurement Methods Evaluation and Development	5,7,8,10,12,13,28*,46*,47,48,62	60
2. Methods Adaptation and Application Studies	2,11*,21,36,45*,22,49	15
3. Measurement and Test Program Reviews	9,26,54	2
4. Sampling and Analytical Support	14,32,42,51	10
5. Preparation of Guidelines and Procedures	1,3,53,57	10
6. Conduct of Symposia and Training	16*,24,29*,33*,44*,58*	3

*Minor task, <100 hours.

1.1 AREA 1: MEASUREMENT METHODS EVALUATION AND DEVELOPMENT

Area 1 tasks encompassed a broad range of topics of current concern in environmental measurement technology. Tasks were undertaken to develop new techniques and evaluate existing methods in the fields of inorganic compound identification, sulfur/SO_x measurement, and particulate emissions assessment. Seven major tasks were performed in the three indicated fields:

1. Inorganic compound identification
    - Task 7 - Inorganic Compound Identification (oxidized species)
    - Task 8 - Sampling and Analysis of Reduced Inorganic Compounds
2. Sulfur/SO_x measurement
    - Task 10 - Coal Sulfur Measurements
    - Task 13 - Understanding SO_3 Data
    - Task 47 - Automatic Sulfur Trioxide Monitor
3. Particulate emissions assessment
    - Task 5 - SASS Train Level 1 Checkout
    - Task 12 - Continuous Flow Impactor
4. Process Measurement Development
    - Task 48 - Analysis Using Ion Chromatography
    - Task 62 - pH and Chloride Electrode Evaluation

In addition, two minor (<100 hours) tasks were performed:

- Task 28 - SASS-SO_2 Tests
- Task 46 - Stepwise Arsenic Process

1.1.1 Major Task Summaries for Area 1

Task 7 - Inorganic Compound Identification--

Task 7 involved one of the most extensive efforts in the program. It was devoted to the study of measurement procedures for inorganic compounds. While this task was broad in its nature, its main goal was to advance the state of the art for identifying specific inorganic compounds in samples of environmental interest. In this first year of work several subtask areas were investigated:

- Literature review - references on compound identification for specific elements (e.g. As, Se, Sb, Hg, Cd, and Zn) were compiled.
- X-ray diffraction - determination of the sensitivity of specific compounds in an environmental matrix were made.
- Infrared analysis - references on IR and FTIR were compiled and a comparison of the two methods made.
- Selective reduction of As^{+3}/As^{+5} - a chemical approach to the selective reduction of As^{+3}/As^{+5} in aqueous environmental samples was investigated.
- Mass thermal analysis - studies were initiated to determine if volatile inorganic compounds could be thermally desorbed from the surface of collected particulate matter.
- Special studies - potentially useful new analytical methods and procedures were cursorily studied.

In addition to these specific areas of research conducted under this task, TRW has supported EPA/IERL programs in the area of advanced inorganic analysis. In this role, TRW was charged with design, testing and application of advanced analysis schemes for the determination of compounds from process streams including FBC bed materials and combustion source emission streams. As an end result TRW developed a comprehensive inorganic compound identification scheme, which has been detailed in a technical manual for inorganic compound identification.

The major accomplishments and conclusions in each of the six subtask areas are discussed in the sections below.

Literature Survey -- The literature survey compiled and organized over 300 journal articles on a wide range of topics. Computer searches for analysis methods for the elements arsenic, barium, beryllium, boron, cadmium, chlorine, copper, fluoride, lead, manganese, mercury, nickel, selenium, tin, vanadium, and zinc were completed. This literature is currently filed by method at TRW. This file was constantly updated during the course of the contract.

X-Ray Diffraction Studies -- The main goal for X-ray diffraction studies performed at TRW was to investigate the analytical capability of a typical commercial X-ray diffractometer to detect small amounts (1-10%) of various materials of environmental interest. Performance of an XRD unit was evaluated by tests on laboratory and field samples.

X-ray diffraction technique is a relatively simple analytical tool widely used for qualitative and quantitative identification of various crystalline compounds present in a amorphous matrix. However, the sensitivity of the X-ray diffraction method is inferior to other methods, and the sensitivity may vary depending on the compound under study and the matrix. Sensitivity tests were therefore run on laboratory samples of pure compounds in an amorphous matrix. Detection limits for numerous inorganic oxides and sulfates were determined from the results of these sensitivity tests. Since sample handling procedures may also affect analytical results, alternate techniques for this procedure were tested.

XRD analyses of industrial samples of FBC fly ash and thermally/chemically treated coal char identified many constituents of these materials successfully. However, because of the overlap of several compounds, unambiguous identification of all spectral lines was not possible. In particular, it was found that the Na_2CO_3 spectra did not correspond to the literature values and hence, identification of it within the samples was impossible. This particular result was nonetheless expected from work by other investigators.

In general, results showed that XRD analysis of environmental samples is possible, but that problem areas still exist. Sample mounting methods need to be developed to either analyze material impacted directly on glass fiber filter without sample modification. One possible technique is to use Freon as the solvent and ultrasonic cleaner to break-up the filter. Filtration or density gradiant separation could be used to remove the glass fibers.

Low sensitivity of XRD compared to other methods of analysis remains a problem. Methods to improve the sensitivity of the XRD technique include use of more sophisticated equipment or computer averaging techniques. The latter method should be further studied.

Infrared Spectroscopy Studies -- In the total compound analysis scheme, infrared analysis can potentially identify anions present in the sample and determine the compound containing the anion.

Technical problems that must be addressed include effect and control of moisture content in the sample. It is expected that the samples will have to be dried to a constant water content to simplify the analysis problem. In preparing samples that contain reactive materials such as bisulfates for IR analysis, KBr should not be used due to possible anion exchange reactions.

A series of IR spectra were obtained for five different flyash samples. These samples were analyzed by conventional IR and FTIR in the mid-IR region. While further work will be needed to identify the bands, the high quality of the spectra and the obvious changes in the position and strengths of various bands shown in the FTIR spectra clearly indicates the utility of FTIR over conventional IR in recognizing changes occurring in the sample. Also, the ability of the FTIR to subtract background spectra can be used to remove unwanted materials. While 40 scans were averaged in this test, 400 or 4000 scans could have been made to improve sensitivity.

Work should be continued on IR to:

- Study the effects of sample conditioning on the structure of the compounds. Work is needed to "normalize" samples so that spectral shifts due to hydration, crystalline form or sample matrix do not occur or are identified.
- Study the direct analysis of material impacted on glass filter to see if this information can be used to supplement direct XRD analysis.
- Study the subtraction capability of FTIR to establish guidelines on subtraction procedures for complex mixtures. The goal is to subtract different samples from each other to emphasize differences in the samples, such as particulate matter collected at the inlet

or outlet of an FGD.

As^{+3}/As^{+5} Speciation -- A procecure was tested to selectively reduce As^{+3}/As^{+5} in aqueous environmental samples to permit separate analysis of each species. A comprehensive test matrix was run to quantify sample recovery and analytical errors in the procedure. Samples containing As^{+3} and As^{+5}, both separately and combined, were analyzed using several different reaction chemistries.

Results showed a favorable accuracy and recovery for As^{+3}; however, recovery of As^{+5} was low. Further work is necessary to find the cause of this low As^{+5} recovery.

Mass Thermal Analysis -- A proposed method to analyze for possible thermal desorption of volatile inorganic compounds from the surface of collected particulate matter using TGA/MS was tested.

It was concluded that this technique is useful in determining the gross thermal characteristics of a sample. For example, a TGA run could provide information as to the amount of moisture in a sample, likely decomposition temperatures of the mixture components, and overall thermal stability. This type of information could be of value in selecting a drying cycle for a mixture prior to analysis. However, determination of small quantities (<1%) of materials does not appear to be very promising unless reproducible results can be obtained from a known mixture. This was not the case for the FBC material.

Special Studies -- Proton induced X-ray emission (PIXE), SEM-EDX, and Electron Microprobe analyses were evaluated as new and potentially important analytical tools in environmental measurement. Specific advantages and limitations for each method were identified. PIXE was found to be useful on some sample types, but would be of limited use as a general analytical tool without extensive modification. SEM-EDX was found to be adequate for high resolution morphology studies of environmental particles. Techniques which warrant further study for their use in elemental depth profiling include Scanning Auger Microanalysis (SAM), ESCA, and SIMS.

Task 8 - Sampling and Analysis of Reduced Inorganic Compounds--

The objective of Task 8 was to develop a sampling and analytical system to determine the emission rate of specific reduced inorganic compounds. The list of reduced compounds included metal hydrides, elements, and non-metal hydrides. The overall goal was a sampling and analysis accuracy of ± 25 percent and a precision of ± 30 percent.

Results in several subtask areas are summarized below.

- Literature survey - The survey suggested a general lack of material on compound identification for reduced inorganic materials. In a few cases, the literature gave specific examples or suggested methods of analysis. These references and methods were given in the final report.
- Laboratory testing - Methods for generation of volatile metal hydrides were tested. These production methods have been established as quantitative and are the first step in evaluating a sampling and analysis procedure. The details of the procedure together with current analysis data have been reported in detail in monthly progress reports.
- Field testing - The SASS train was tested for its suitability for sampling reactive inorganic species for subsequent compound identification. Sampling for solid inorganic species from particulate material may be possible using the SASS, however, reduced inorganic gases will either be lost or chemically modified due to their inherent susceptibility to oxidation.

Task 10 - Coal Sulfur Measurements--

A need existed for a more accurate procedure for analysis of organic sulfur in coal. As part of Task 10, TRW proposed two entirely new coal organic sulfur analysis procedures, both based on the selective removal of organic sulfur species present in coal via selective oxidation in an oxygen plasma instrument. The first procedure entailed the determination of organic sulfur by difference between two highly accurate and precise $BaSO_4$ gravimetric procedures: one performed on the starting coal and one performed on the resultant ash from an oxygen plasma decomposition of the coal matrix. The second procedure is the direct determination of organic sulfur by collection of SO_2/SO_3 on solid sorbents placed in the outlet line from the plasma asher.

Organic sulfur analyses using the indirect gravimetric procedure were compared with results obtained on aliquots of the same coals using standard ASTM D2492 procedures with pyritic sulfur being determined using both the alternate atomic absorption (AA) technique and the standard titrimetric procedure. The results showed that both the plasma ashing and the ASTM-AA procedures gave consistent results, while the ASTM titrimetric procedure gave widely discrepant results that tended to be significantly low for untreated Appalachian coals. Thus, in reference to evaluation of coal cleaning processes, it appears that the ASTM procedure gave results that were virtually independnet of the past history of the coal.

The direct organic sulfur analysis technique via sorbent trapping of evolved SO_x species during plasma ashing was shown to be a viable technique. Not only could this technique be used for organic sulfur but the concept could be expanded to include other organically bound species such as I, Cl, and nitrogen. However, the physical limitations of currently available plasma ashing systems are incompatible with the proposed technique. This is an engineering problem and could be solved by redesigning currently available ashing chambers.

Task 13 - Understanding SO_3 Data--

The objective of this task was to develop a stack sampling procedure for the measurement of the mass emission rate of sulfuric acid within a precision of ±10% but not to exceed ±20%. Subtasks were devoted to the selection and testing (laboratory and field) of the H_2SO_4 sampling train.

Sampling and analysis systems were evaluated on the criteria of selectivity, sensitivity, accuracy, precision, ease of operation, and reliability. The controlled condensation system (CCS) developed by Goksoyr and Ross was selected for additional study over the selective absorption system which is the basis of EPA Method 8.

Laboratory and field tests showed that:

- The accuracy of the CCS, both in the laboratory and in the field, was acceptable.

- No significant oxidation of SO_2 occurred on the filter to the CCS.
- Coal fly ash on the filter did not catalyze SO_2 oxidation in the CCS, but did reduce the amount of H_2SO_4 collected.
- The coefficient of variance of the H_2SO_4 output at the coal-fired utility tested was estimated to be ±65%. This high CV_S implies that to obtain a good average H_2SO_4 value from this type of source, it will be necessary to take a large number of samples spread out over a period of days.

Task 47 - Automatic Sulfuric Acid monitor --

The objectives of this task were to design, construct, and test an automatic sulfur trioxide monitor based on the Goksoyr-Ross coil capable of providing reasonably accurate measurements (±20%) of sulfuric acid concentration in process streams.

The unit was designed to be sturdy and easy to operate in the field, with the capability to operate unattended for continuous periods on the order of 24 hours. Provisions to easily modify the unit were part of the design.

A field test unit was constructed and laboratory tests completed. The unit operated continuously for 11 hours and its results compared favorably with manual CCS measurements that were made.

Task 5 - SASS Train Level 1 Checkout--

The performance of one of the first SASS trains was evaluated during tests conducted on board the incinerator ship M/T Vulcanus. Results of these tests were used to evaluate analytical procedures set forth in the first IERL-RTP Level 1 manual.

Problem areas for further study under other tasks and contracts were identified in Task 5. These solution-oriented studies, conducted after completion of Task 5, eventually led to refinements of the Level 1 procedures such as the quartz-lined Parr bomb method. These refinements have all been addressed and the resulting recommended Level 1 modifications assembled as TRW's input to the Level 1 revisions under Task 5.

Task 12 - Continuous Flow Impactor--

Task 12 was a pioneering effort to develop a continuous flow impactor based on a concept first suggested by TRW. The purpose of the task was to determine the feasibility of an impactor in which the collection "surface" is the interface between two opposing jets.

A test unit was designed, constructed, and laboratory tested. Basic proof-of-principle tests on the unit were successful, demonstrating a technically viable and field acceptable hardware concept. Performance of the unit is expected to be comparable to presently available staged impactors.

Refinements to the prototype unit were investigated, with the following results:

- Preliminary design studies indicate that a staged impactor can easily be integrated into a sampling probe to perform in-situ particulate size distribution measurements.
- Feasibility of a simple optical system compatible with the in-situ sampling hardware was shown analytically.
- The continuous flow impactor has a potentially greater accuracy capability than standard impactors since it inherently avoids the traditional problems of particulate bounce and reentrainment.

Potential applications for the continuous flow impactor include control device evaluation, continuous monitoring of particulate emissions for regulatory purposes, and collection of particles in an inert atmosphere to quench chemical reactions. Based on the results of this task, further testing of the laboratory unit and the proposed optical system is recommended. Subsequently, development of a field-worthy instrument should be undertaken.

Task 48 - Analysis Using Ion Chromatography--

This task involved the development of an analytical scheme using ion chromatography to determine specific ions in lime/limestone wet scrubbers and in dual-alkali process streams. Working with synthetic mixtures and actual samples from the Tennessee Valley Authority Shawnee Test Facility at Paducah, Kentucky, TRW staff developed procedures for 1) sample collection; 2) sample preservation; and 3) the separation of solutions, slurries, solids and solubles in cake. The accuracy and precision of this new analytical scheme was shown and a detailed analytical procedures manual was written. Methods for the qualitative and quantitative analysis of sodium, potassium, magnesium, calcium, chloride, total oxidizable sulfur, sulfate, sulfur, nitrate, carbonate and hydroxide were emphasized.

Task 62 - pH and Chloride Sensitive Electrodes--

This task was an outgrowth of a symposium attended by representatives of the EPA, TRW, TVA and the University of Cincinnati. One of the concerns expressed was the applicability of chloride and pH electrodes in automated systems controlling aspects of flue gas desulfurization units operations. An initial survey of 8 utilities showed chloride measurements were of interest only where high concentrations were found. On the other hand, all facilities relied on pH measurements to monitor the operation of the FGD.

The second part in this task was an evaluation of the performance of self-cleaning electrode and a standard pH electrode. Comparing these two with one another, as well as with a laboratory pH electrode and meter setup, revealed the following:

- The accuracy and precision of the self-cleaning and standard type electrode.
- Scaling was a confirmed maintenance problem with the standard type electrode.
- Clogging of the screen surrounding the electrode was a maintenance problem with the self-cleaning electrode used in slurry streams.
- For continuous periods of operation greater than two weeks in slurry streams, the self-cleaning electrode required slightly less maintenance.

1.1.2 Minor Task Summaries

Two tasks in Area 1, Measurement Methods Evaluation and Development, required less than 100 hours for completion. The first, Task 28 (SASS-SO_2 Tests) was an investigation to determine if the SASS train condensation modules could be used to collect H_2SO_4 while avoiding a large positive error due to SO_2 oxidation in either gas or liquid phases. Oxidation of sulfur species in the SASS train was quantified, the results indicating that use of the SASS train to measure H_2SO_4 was not appropriate.

Task 46 (Stepwise Arsenic Process) evaluated the proposed Level 1 arsenic procedure based on atomic absorption spectrometry in terms of its accuracy, precision, percentage recovery and efficiency of usage. The results of the task identified the most reliable techniques of analysis and quantified the level of accuracy and precision which could be expected from the proposed procedure.

1.2 AREA 2: METHODS ADAPTATION AND APPLICATION STUDIES

Tasks in Area 2 were designed to investigate new applications for existing methods in process stream sampling and analysis. New applications for both hardware and software were developed and tested. Applications included process measurements at two FGD facilities, computer modeling of test data, prediction of the utility of Level 1 methods in assessing MATE levels of inorganic MEG compounds, and flow measurement evaluation studies. Five major tasks were performed:

- Task 2 - Limestone FGD Demo Support
- Task 21 - Test Data Modeling
- Task 22 - Evaluation of Dry Sorbents and Fabric Filtration for FGD
- Task 36 - Inorganic MEG Compounds and Level 1 Assessment
- Task 49 - NIPSCO Mass Emission Monitor

1.2.1 Major Task Summaries

Task 2 - Limestone FGD Demo Support--

Methods of sizing dry aerosols and measuring SO_3 were applied to characterizing influent and effluent gas streams from a Flue Gas Desulfurization (FGD) unit. The sizing method for the dry particulate matter entering the FGD process was selected by the EPA to be a manual technique utilizing a Brink Impactor. A manual system for the FGD process effluent stream was chosen on the basis of a literature survey, contacts with experts in the field, and an evaluation of available information. The method chosen was the Meterology Research, Inc. Cascade Impactor used out of stack. Finally, a method for SO_3 (H_2SO_4 vapor) was developed based on the Controlled Condensation (Goksoyr/Ross) method and was successfully tested under laboratory conditions. In addition to these method adaptation and application areas, on-site training and support were provided by TRW personnel and a procedures document for FGD process measurements was prepared.

Quality assurance activities under Task 2 were extensive. In the procedures document describing the aerosol sizing and SO_3 sampling procedures, information was provided on 1) equipment care and usage; 2) guidelines for laboratory techniques; 3) specific critical area checklists for each procedure; 4) data interpretation aids to monitor the quality of the results achieved; 5) specific maintenance and calibration schedules; and 6) troubleshooting and repair schemes.

In addition to this documented quality assurance activity, an on-site training session was given to train the TVA personnel on the use of all the equipment and procedures. Throughout the program, senior TRW personnel were available for consultation over the phone or for troubleshooting in the field.

Based on the Task 2 work, it was recommended that:

- Continued on-site and verbal assistance be provided to the Shawnee Test Facility in the area of trace element sampling and analysis.
- Support be given to improve process measurement at the FGD units.
- New control strategies be developed based on improved process measurement of such species as $SO_4^=$, $SO_3^=$, Ca^{+2}, and Mg^{+2}.

Task 21 - Test Data Modeling--

The objective of this task was to develop test (computer) models which permit a chemist to evaluate, a priori, and the variation in his test results using assumptions based on his experience.

The computer program developed answered the following questions:

- A chemist will take either 2 or 3 samples (replications) for a particular test. What kind of results can be expected? To evaluate the results the analyst can input either a ± range or the actual σ along with the nominals.

- A chemist has three populations of known mean and standard deviation (or ± percent range) values. What are the mean and standard deviation values of a new population defined as sums of three samples, one from each of the three original populations?

- A chemist again has three populations of known mean and standard deviation (or ± percent range) values. The populations are now comprised of the original unknown (or summation) population and any two of the three originally known populations which define the summation population. What are the mean and standard deviation values of the remaining third original population (presently unknown)?

Task 22 - Evaluation of Dry Sorbents and Fabric Filtration for FGD--

This study, which was an extension of preliminary work on the dry sorbent baghouse FGD concept done in 1976, encompassed six aspects of fabric filtration with simultaneous SO_2 removal by dry sorbents:

1) Calculation of the cost of a baghouse and the associated sorbent system.

2) Calculation of the cost of the disposal options.

3) Estimation of the sorbent cost, including mining cost for nahcolite, cost of trona and a sensitivity study of cost versus quantity.

4) Sensitivity studies of operating costs and annualized costs versus such parameters and assumptions as sulfur content and boiler size.

5) Recommendations for parameters and ranges to use in a test program.

6) Feasibility of using Mag-Ox as a sorbent.

The cost estimates conformed to the methods and terminology used in the TVA FGD Process Cost Study (completed in 1974 and revised in 1976).

Task 36 - Inorganic MEG Compounds and Level 1 Assessment--

This task was initiated to theoretically predict:

- If Level 1 Environmental Assessment is capable of detecting the inorganic Multimedia Environmental Goal (MEG) compounds and elements at their Estimated Permissible Concentrations (EPC).*

- Where in the Source Assessment Sampling System each inorganic compound and element is likely to be found.

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*The original task effort was redirected to substitute Maximum Acute Toxicity Effluent (MATE) levels for EPCs.

- What MEG compounds, elements and valence states can be predicted in Level 1 aqueous samples.
- The nature of difficulty in detecting MEG compounds at EPC levels by "non-Level 1" techniques.

Organometallic MEG compounds were not included in this study.

After analyzing the capability of Level 1 to detect MEG compounds and elements, actual Level 1 data were assessed to compare values obtained and limits of detection with MATE Levels (EPCs).

Conclusions arising from the Task 36 effort were:

- The Level 1 Environmental Assessment protocol is capable of detecting most MEG elements at the concentration levels imposed by the EPC X 100 criteria.
- Beryllium at the EPC X 100 level of interest is theoretically not detectable by current Level 1 techniques.
- Arsenic, selenium, thallium, chromium, silver, lithium, antimony and cadmium are theoretically not detectable at the EPC X 100 level of interest in some of the SASS components.
- Detectability problems have not yet been encountered for MEG elements at coal-and oil-fired systems sampled.
- In water samples, beryllium and arsenic at EPC X 100 levels of interest are not detectable by current Level 1 techniques.

Task 49 - Mass Emissions Monitor Demonstration--

In this task, hardware and methodology for continuous high and accuracy flow and gas composition measurements in large stationary source stacks and ducts were to be demonstrated. Prior work sponsored by the EPA had produced a multiple point gas sampling probe which showed potential for greatly enhanced accuracy over single point continuous sampling techniques without a substantial cost or maintenance impact. Agreement was reached with the NIPSCO power plant in Gary, Indiana to test a new wet scrubber and to even use Dieterich Standard Annubars, a multiple point pilot tube probe already installed in the stack for volumetric flow measurements. The field effort was severely hampered by scrubber downtime or by sampling system downtime. Limited data did reveal significant compositional stratification at the test site.

1.2.2 Minor Task Summaries

Two minor (<100 hour) tasks were performed under Area 2, Methods Adaptation and Application Studies. In Task 11 (Mass Emission Monitor Demo), an industrial site was selected to demonstrate the application of continuous flow measurements, gas sampling hardware, and methodologies.

From a thermodynamic analysis of the SASS train thermal control system, a design and cost estimate for an alternate system was developed, as part of Task 45 (SASS Train Thermal Control Alternate).

1.3 AREA 3: MEASUREMENT AND TEST PROGRAM REVIEWS

Area 3 task objectives were to assess the validity and accuracy of measurement methods in environmental sampling and analysis technology. Critical reviews were made of existing methods for measuring coal mass flow, composition and total mass emissions from stationary sources, and the fate of PCBs at a plant fire. Two major tasks were performed:

- Task 9 - Coal Monitoring Instrumentation
- Task 26 - Total Particulate Mass Emission Sampling Errors

1.3.1 Major Task Summaries

Task 9 - Coal Monitoring Instrumentation--

The purpose of the task was to investigate the state of the art for continuous coal mass flow and composition measurements, both to determine current capabilities, and to investigate the need for EPA involvement in research and development efforts. The types of flow investigated were dry coal flow (typically on a belt) and wet coal slurry flow. Composition-type measurements are performed on small samples (few grams) with laboratory instruments and on dry slipstreams with various instruments currently under development. Measurement in slurries is presently limited to only slurry density.

Based on the results of a literature search, vendor and user contacts, and a field trip, information was obtained on coal measurement instrumentation, both available and under development. Information compiled along with user data was then used to compare the various instruments. Additional calculations and analyses were performed by TRW to determine system limitations and errors. A final report, in the form of a technical manual, was prepared.

Some of the major conclusions of Task 9 were:

- Weight belt devices, either electromechanical or nuclear, and electromagnetic flow meters (typically coupled with nuclear density gages) are the most used devices for dry coal flow measurement and wet coal slurry flow measurement, respectively, and will be acceptable for most situations.

- Development of neutron activation instruments is proceeding well, with a sulfur meter expected as a production item within the next few years. Hopefully, this will be followed by modified versions capable of determining moisture and heating value. Neutron activation devices are of particular interest because they hold the promise of sampling entire coal streams, thus eliminating the major problem with present equipment - that of obtaining a representative sample of small quantity.

- The most reasonable area for IERL investigation in the near future is how to make the best uses of available and soon-to-be-available instrumentation to control the operation of stationary sources. Such control could minimize pollutant emissions through direct combustion control and/or optimizing operation of devices such as wet scrubbers. The greatest ultimate value of coal monitoring instruments is not as monitoring sensors, but as components in an active control system, either on sources of direct coal combustion, or in coal cleaning plants.

Task 26 - Total Particulate Mass Emission Sampling Errors--

The task objective was to determine the accuracy of particulate mass emissions as determined by techniques in "IERL-RTP Procedures Manual: Level 1 Environmental Assessment."

A standard error analysis was performed based on the assumption of a fully entrained particle model with a factor to allow for gas-particle slip. Error equations were derived, and individual error terms were evaluated using instrument characteristics, typical source characteristics, and methodology details.

The major conclusion of the Task 26 study was that the SASS train and Method 1 procedures are sufficiently accurate as Level 1 methods. Additional conclusions were:

- A SASS train operated in accordance with "IERL-RTP Procedures Manual: Level 1 Environmental Assessment" sampling at a single point will have a sampling accuracy of a factor of ±2 or better in most locations such as stacks or control device inlets. Under worst case conditions, such as at an ESP outlet, it will have an accuracy of about a factor of ±3, due to stratification.
- In single point sampling, the mapping error (non-representativeness of the selected point) will be the largest individual error in the system. By using a 16-point traverse rather than sampling at a single point, stratification errors are minimized. Using this method, sampling accuracy of the SASS train could be improved to about ±25 percent.
- Additional stratification data should be obtained at sites such as full-scale, coal-fired power plants for important locations: control device inlets, control device outlets, and stacks. Such data should be used for the development of single point sampling methodology.
- Results suggest that for hardware of a given accuracy, there will exist specific procedures to optimize system performance (achieve close to maximum accuracy while minimizing manpower requirements and sampling times). Work should be continued to prepare an IERL-RTP Procedures Manual in this area.

1.3.2 Minor Task Summaries

One minor (<100 hours) task was performed in Area 3, Measurement and Test Program Reviews. In Task 54, Fate of PCBs in Rollins Plant Fire, the objective was to investigate the fate of polychlorinated biphenyl compounds (PCBs) that were stored in a tank farm on a chemical disposal site when a disastrous fire occurred in December, 1977. The primary question was what new environmentally hazardous products may have been formed under the conditions existing at the time of the accident.

This study concluded that under certain conditions polychlorinated biphenyl compounds may serve as precursors for the formation of other environmentally undesirable compounds. The most probable class of compounds formed are dibenzofurans. The reaction pathways to these compounds seemed to be favorable under oxygen deficient combustion conditions and low temperature. Conversely, it seems improbable that dibenzo-p-dioxins are formed under similar conditions. If dibenzo-p-dioxins were to be formed, they would come from the dibenzofurans that are initially generated from the PCBs. Formation of polycyclic aromatic hydrocarbons (PAH) is possible via pyrolysis of PCBs in oxygen deficient conditions that could have existed in the Rollins fire.

1.4 AREA 4: SAMPLING AND ANALYTICAL SUPPORT

TRW provided various kinds of support to several Level 1 assessment activities by other contractors under three major Area 4 tasks. TRW provided on-site sampling/analysis assistance, laboratory analysis of split samples, consulting services, quality assurance and logistical support. The following specific tasks were completed:

- Task 14 - KVB Test Support
- Task 32 - Support to Level 1 Environmental Assessment Study (Radian)
- Task 42 - Support Services to Level 1 Environmental Assessment Performance Evaluation
- Task 51 - EPA/TVA Limestone FGD Support

1.4.1 Major Task Summaries

Task 14 - KVB Test Support--

TRW supported KVB Engineering in a Level 1 sampling effort on an experimental coal-fired boiler at KVB's Tustin, California facility. TRW services were required for:

- Determining the adequacy of the sampling test as a Level 1 Environmental Assessment in accordance with the draft copy of the Level 1 Procedures Manual.
- Answering any questions from KVB which might arise concerning the requirements on the draft IERL procedures manual.
- Analyzing samples in accordance with the Level 1 procedures in parallel with KVB's analytical subcontractor, Calspan.

The emphasis in the use of the data generated under this task was on the mass balance. In this regard, the SASS was an effective unit performing well within the Level 1 error limits of a factor of 2-3. The cumulative percentage differences between the SSMS values and the special case analyses values for total quantities trapped in the SASS train, and for the theoretical ideals for baghouse and coal feed, all showed excellent reproducibility in terms of precision. The SSMS technique proved more reliable than AA or colorimetry for As, Hg and Sb because of the lower detection limits for SSMS.

Task 32 - Support to Level 1 Environmental Assessment Study--

TRW was assigned by PMB to assist, advise, and instruct Radian Corporation in conducting a Level 1 Environmental Assessment (EA) of a low BTU coal gasification pilot plant at the Holston Army Ammunition Arsenal. Under this task, TRW provided instruction to Radian personnel on Level 1 procedures, on-site sampling and analysis support, and basic quality assurance and consulting services. In addition to merely consulting, TRW used its involvement in this task to contribute to the overall development of Level 1 methodology.

Task 32 was important in that it provided a necessary evaluation mechanism for the Level 1 EA protocol as applied to a source of unusually high organic content. Invaluable experience was gained in this teamed effort, which provided an excellent blend of sampling and analytical expertise. Future teaming activities are strongly recommended.

Task 42 - Support Services to Level 1 Environmental Assessment Performance Evaluation--

Task 42 was part of TRW's participation with RTI, ADL, Radian, and SoRI in collaborative testing to define the precision of the SASS and the Level 1 analysis procedures.

The overall project was divided into two phases. Phase I, field sampling, assessed SASS performance and Level 1 field analysis procedures at an aluminum smelter. Phase II efforts were directed at the Level 1 laboratory analysis procedures. TRW assisted in Phase I with logistical and manpower support for the on-site sampling effort (including pretest site survey), and in Phase II with analytical laboratory support.

Although remarkable progress has been made toward defining the details of the Level 1 procedures in the relatively short period of time since they were first published, considerable ambiguities remain which can lead to differences in the interpretation of the procedures. That such differences exist was evident in both phases of the effort. The seriousness of these potential interpretive differences will hopefully be addressed in RTI's summation of this collaborative testing.

Task 51 - EPA/TVA Limestone FGD Support--

This task involved providing support to process measurement activities at the EPA Shawnee Wet Limestone Test Facility in Paducah, Kentucky. Five major concerns have been investigated: recommending particle sizing and trace elements analysis approaches; reviewing and recommending sampling techniques and analysis methods for trace elements and compounds; recommending sampling procedures to identify sulfur forms; evaluating the feasibility of sampling liquid aerosols at a mist eliminator; and developing automated methods to measure scrubber process stream parameters, thereby improving control of the scrubber operation. Each problem was addressed either at a briefing or in a research report.

1.5 AREA 5: PREPARATION OF GUIDELINES AND PROCEDURES

TRW efforts in Area 5 have involved parallel efforts in the preparation and revision of the EPA publication "IERL-RTP Procedures Manual: Level 1 Environmental Assessment" and in the development and evaluation of Level 1 analytical procedures. The following major tasks were grouped under Area 5, although guidelines and procedures were prepared to some extent under many other tasks.

- Task 1 - Level 1 Manual Revision/Project Start-Up
- Task 3 - Support to Ocean Incineration
- Task 53 - Input to Level 1 Manual Revision
- Task 57 - At-Sea Incineration Environmental Impact Statement

1.5.1 Major Task Summaries

Task 1 - Level 1 Manual Revision/Project Start-Up--

The objective of this task was to incorporate review comments on the draft manual: "IERL-RTP Procedures Manual Level 1 Environmental Assessment," describing methods for conducting Level 1 environmental assessment. The draft was prepared under EPA Contract 68-02-1412, Task 18. The final revised manual was prepared under this task. Because this was the first task under this contract, project start-up costs were also incorporated into it.

Task 3 - Support to Ocean Incineration--

The technical objectives of this task were to:

- Evaluate at-sea incineration processes for the destruction of chemical waste products, especially chlorinated organic materials, on board the Matthias III and M/T Vulcanus incinerator vessels.
- Develop guidelines for incinerator design, operational controls, monitoring methodology and acceptance criteria to be utilized by EPA and IMCO in establishing at-sea incineration permit requirements.

Operational, performance and emissions data were obtained by TRW sampling teams for a series of burns on the Matthias III and on the M/T Vulcanus. Based on these incineration data, TRW assisted EPA in generating technical considerations and guidelines to be utilized in international agreements on control of incineration at sea. EPA subsequently submitted these recommendations to the IMCO Intersessional Working Group for Incineration at Sea at their London, England meeting. These guidelines will also be used to establish U.S. regulations.

Task 53 - Input to Level 1 Manual Revision--

This task was initiated in November 1977, to provide updated and revised chapters on gas, vapor and particulate sampling, and inorganic analysis (Chapters II, III, and VII). These revised chapters were submitted to Research Triangle Institute (RTI) to be incorporated into the republication of the IERL-RTP Procedure Manual for Level 1 Environmental Assessments.

The revised chapters submitted under this task represented the best currently available Level 1 methodology. Specific tasks conducted on this contract and the Environmental Assessment of Conventional Combustion Sources (EACCS) project examined and improved the inorganic analysis procedures, and the over 50 Level 1 source tests performed on the EACCS project provided practical experience in dealing with the requirements and realities of field testing. These experiences in both the analytical and sampling aspects of Level 1 methodology had been integrated into the EACCS procedures manual as they evolved. With this task, these improvements also became part of TRW's input to the revision of the IERL-RTP Level 1 manual.

Task 57 - At-Sea Environmental Impact Statement Studies--

The objective of this task was to prepare portions of an environmental impact statement for at-sea incineration of industrial wastes documenting the effects on the environment which could result from the adoption of international standards regulating incineration at-sea activities.

The results of this effort were presented to the International Maritime Consultative Organization at their June 1978 conference in London.

1.6 AREA 6: CONDUCT OF SYMPOSIA AND TRAINING SESSIONS

Six tasks in this program were devoted to TRW participation in symposia or presentations related to the TLE program. Only one, Task 24 (Process Measurement Symposium) required more than 100 hours labor. Two of the symposia covered the general topic of environmental/process measurements; the other four dealt with specific measurement techniques.

1.6.1 Major Task Summary

Task 24 - Process Measurement Symposium--

This task was devoted to the preparation and implementation of the Symposium on Process Measurements for Environmental Assessments. The conference was designed as a forum to present, discuss and evaluate measurement requirements, approaches and results within the broader context of the entire Environmental Assessment Program area. Considering the wide-ranging scope of the Environmental Assessment Program area, a broad cross section of industry and government were invited to participate in the conference proceedings and discussions.

The Symposium Staff consisted of two members from EPA; Ms. Brenda Foil and Ms. Susan Sharpe, and three members from TRW; Ms. Mary McKay, Mrs. Linda Rosenfeld and Mr. Chuck Weekley. The overall coordinator for the Symposium was Dr. Eugene Burns and the Symposium General Chairman was Mr. James Dorsey. Papers were presented by the following TRW personnel: R. F. Maddalone and L. E. Ryan (Inorganic Emissions Measurements), J. W. Hamersma (Process Measurements of Conventional Combustion Systems), and J. E. Cotter (Environmental Measurements Program at the Paraho Shale Oil Recovery Facility).

1.6.2 Minor Task Summaries

Under Task 16 (NBS Meeting), a TRW representative attended the National Bureau of Standards symposium on "Methods and Standards for Environmental Measurement." Papers were presented in the following areas:

- Single and multielement technique development
- Physical and chemical characterizations of aerosols
- Organometallic sampling and analysis
- Laser sensing methods
- Environmental standards

Task 29 (SO_3 Measurement Presentation) was a training session given by TRW to IERL contractors on the methodology to measure H_2SO_4 in particle laden flue gas streams. The presentation covered the use of the controlled condensation procedure in the field and presented laboratory data from Task 13.

Under Task 33 (Denver X-ray Meeting), a TRW representative attended the Denver Symposium on "Applications of X-Ray to Environmental and

Occupational Health Analyses." The Symposium was sponsored by the Denver Research Institute, University of Denver and Phillips Electronic Instruments. Papers were presented on the following instrumental methods of analysis:

- X-Ray Diffraction
- Electron Microprobe
- Electron Microscopy

Under Task 44 (Particulate Measurement Meeting), a TRW representative attended the "Symposium on High Temperature, High Pressure Particulate Control," in Washington, D. C., sponsored by EPA/DOE. Of special interest were the presentations given in Session IV: Particle Sampling and Measurement. With regard to particulate control technology, it was made clear that while there are various proposed techniques, none are yet fully proven and operational.

Task 58 involved TRW's participation in the workshop on Measurement Technology and Characterization of Primary Sulfur Oxides Emission from Combustion Sources, sponsored by the Environmental Sciences Research Laboratory, EPA/RTP, during April 1978. Dr. R. F. Maddalone presented a paper, "Sulfur Emissions Sampling and Analysis," detailing work to improve techniques for sampling and analysis of SO_2, H_2SO_4 and particulate sulfate emissions from flue gas desulfurization units.

SECTION 2

MAJOR TASKS

2.1 TASK 1 LEVEL 1 MANUAL REVISION/PROJECT START-UP

2.1.1 Objective

The objective of this task was to incorporate review comments on the draft manual: IERL-RTP Procedures Manual Level 1 Environmental Assessment, describing methods for conducting Level 1 environmental assessment. The draft was prepared under EPA Contract 68-02-1412, Task 18. The final revised manual was prepared under this task. Because this was the first task under this contract, project start-up costs were also incorporated into it.

2.1.2 Approach

The basic draft document was prepared under EPA Contract 68-02-1412, Task 18. The objective of this task was to devise a cost effective set of sampling and analytical procedures for Level 1 of the phased approach to environmental assessment programs. This document presented for the first time an integrated set of sampling and analytical procedures for environmental assessment programs. As such, it was subjected to a detailed review in June 1976 with representation of the Process Measurement Branch, IERL/RTP and five other TLE contractors including Arthur D. Little, Inc., Aerotherm/Acurex Corp., Research Triangle Institute, Southern Research Institute and The Research Corporation of New England. Based upon these discussions, a new revision of the manual was prepared and submitted to EPA in July 1976. This draft and further revision was discussed with Dr. R. M. Statnick during August 1976. The final draft was published in September 1976.

This task also served as the project start-up task. Under this portion of the work, the project was organized, people assigned, task orders initiated and a task work plan prepared.

2.2 TASK 2 LIMESTONE FGD DEMO SUPPORT

2.2.1 Objectives

The technical objective of this task was to prepare a series of procedure documents for sizing dry aerosols and measuring SO_3 entering and leaving a Flue Gas Desulfurization (FGD) unit and written for GS-4 personnel or equivalent. The sizing method for the dry particulate matter entering the FGD process was selected by the EPA to be a manual technique utilizing a Brink Impactor. A manual system for the FGD process effluent stream was chosen on the basis of a literature survey, contacts with experts in the field, and an evaluation of available information. The method chosen was the Meteorology Research Inc. Cascade Impactor used out of stack. Finally a method for SO_3 (H_2SO_4 vapor) was developed based on the Controlled Condensation (Goksoyr/Ross) method and was successfully tested under laboratory conditions. In addition to these method development areas, on-site training and support was provided by TRW personnel.

The task was divided into three areas of effort:

1) Aerodynamic Size Distribution Measurement of Dry Aerosols
2) Procedure for Sampling and Analysis of SO_3
3) Quality Assurance

2.2.2 Approach

Aerodynamic Size Distribution Measurement of Dry Aerosols--

Documents were prepared describing the methods for determination of the size distribution of dry particulate matter at the inlet and outlet of a flue gas desulfurization (FGD) process. The FGD process inlet measurement system was a Brink Impactor while the outlet measurement system, which must be suitable for extremely low grain loading, was selected from several candidate systems.

The selection of the outlet impactor system was based on the following criteria:

- Ease of assembly and operation - GS-4 level technicians should be able to operate the instrument.
- Ease of sample recovery - Sample removal should be accomplished under field conditions with minimum of effort.

- Construction material compatibility with sample and sampling environment - The equipment should not corrode or in any way contaminate the sample.
- Sampling period required for sample collection - Flow rates should be maximized to collect adequate amounts of sample for measurement in a reasonable sampling period under low grain loading conditions.
- Sample capacity - The system should be flexible enough to accurately size and collect particulate under high and low grain loadings.
- System design to minimize wall losses and re-entrainment - All samples should be deposited in collection trays or cups.

Applying these criteria, the MRI impactor was selected. Procedure documents describing the operation of the Brink and MRI impactors were written and compiled in an overall procedure manual. This document included: equipment lists, equipment assembly and preparation, on-site set-up and operation, sample removal and handling procedures, and sample weighing procedures. Other than making reference to known procedures (such as EPA Methods 1 through 4), this document was designed to stand by itself and be directed toward GS-4 or equivalent personnel.

Procedure for Sampling and Analysis of SO_3--

A procedure to sample and analyze for SO_3 in flue gas prior to and after FGD process was written. From TRW's knowledge of the SO_3 sampling problem, the Controlled Condensation (Goksoyr/Ross Coil), Brink Impactor and selective liquid impingement appeared to be the methods available. A literature evaluation of the systems was based on the following criteria:

- Sensitivity
- Selectivity
- Precision
- Accuracy
- Efficiency
- Ease of Operation
- Reliability/Maintainability
- Sample Recovery for Analysis

As a result of this evaluation the Controlled Condensation system was tested in the laboratory simulating the conditions in the FGD unit, and found to be precise and accurate.

Quality Assurance--

This effort was devoted to develop methods that will ensure the overall quality of the data taken in the above procedures. Included in the specific QA activities are:

- Critical checkpoint lists for each procedure
- Data validation procedures
- Maintenance schedules
- Troubleshooting procedures
- On-site assistance

2.2.3 Technical Discussion

Originally it was planned that a procedure for liquid aerosol sampling would be developed. The initial recommendations were to use a KLD liquid droplet aerosol counter. Previous experience at Shawnee with the KLD device was positive, but some development work was expected. The main problem with the device was the initial cost (∿$12K). Consequently an alternate approach was suggested and tested in the field. This approach used a Brink impactor and a BMS-11 oven system to maintain isothermal conditions throughout the sampling system to prevent incorporation or condensation of moisture from the gas phase. The liquid aerosols collected would be measured using an automated Karl Fischer analyzer after the collection cups were rinsed with methanol.

In practice, temperature control proved to be very difficult with the BMS-11 oven. A technical decision was made to discontinue this approach. Concurrently, interest in the liquid aerosol sampling tests decreased, so this requirement was deleted. The following sections briefly describe the particulate sampling and SO_3 sampling systems.

Brink Impactor System--

The Brink impactor was used for the determination of the aerodynamic size distribution of dry solids prior to the flue gas desulfurization (FGD) unit. The Brink impactor with a specially designed internal cyclone provided aerodynamic size distribution information between 0.3μ to 10μ in 6 distinct cuts. The recommended flowrate was 0.01 to 0.08 cfm.

This procedure used the Brink impactor out of stack to sample the particulate from the gas stream entering the wet scrubber. After the large particles have been removed from the gas stream by the internal Brink cyclone, the remaining particles in the gas stream are then separated by a Brink Cascade impactor. By weighing each stage of the Brink impactor, the aerodynamic size distribution was determined. Figure 1 shows the Brink impactor and the associated support equipment.

The choice to out-of-stack sample with both the Brink and MRI was made in order to heat the impactors at temperatures (∿175°C) to minimize H_2SO_4 collection. In-stack heating could not accomplish this, so the choice was made to go out of stack.

Control of the Brink was maintained by monitoring the ΔP across the impactor using a magnehelic gauge. This procedure was much more accurate than the Hg manometers used in the BMS-11.

Particle bounce was minimized by coating the collection stages with Aprezon H. This grease was tested in the laboratory and in the stack and showed little or no weight gain or loss under the specified sampling conditions.

MRI Impactor System--

This method is applicable for determining aerodynamic size distribution of dry solid particles emitted from the TVA Shawnee flue gas desulfurization (FGD) processes at a mass loading of 0.07 g/m^3 (0.03 gr/cfm).

The Meteorology Research Inc. (MRI) Inertial Cascade Impactor is designed to measure the aerodynamic size distribution between 0.3 and 30 microns suspended in industrial gas streams at temperatures up to 200°C (392°F) at a flow rate of 0.1 to 0.8 cfm.

As explained in the Brink procedure, out-of-stack sampling was selected to allow higher operating temperature to minimize H_2SO_4 fallout. Heating of the MRI impactor as with the Brink was accomplished using specially fabricated Glass-Cole heating mantles. Aprezon H greased impactor stages were used to prevent particle bounce. Figure 2 shows the equipment set-up for the MRI.

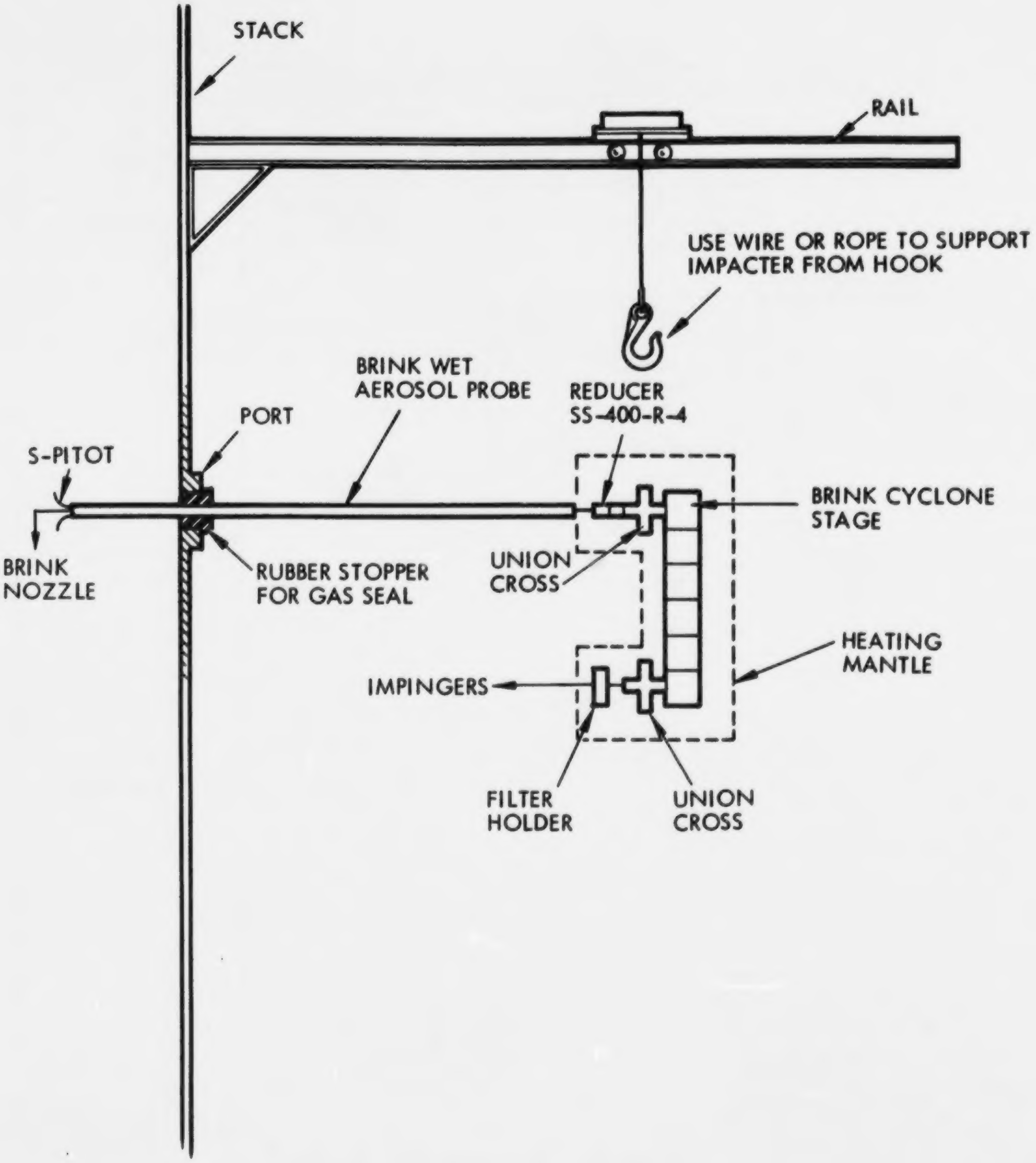


Figure 1. Brink Impactor Set-Up

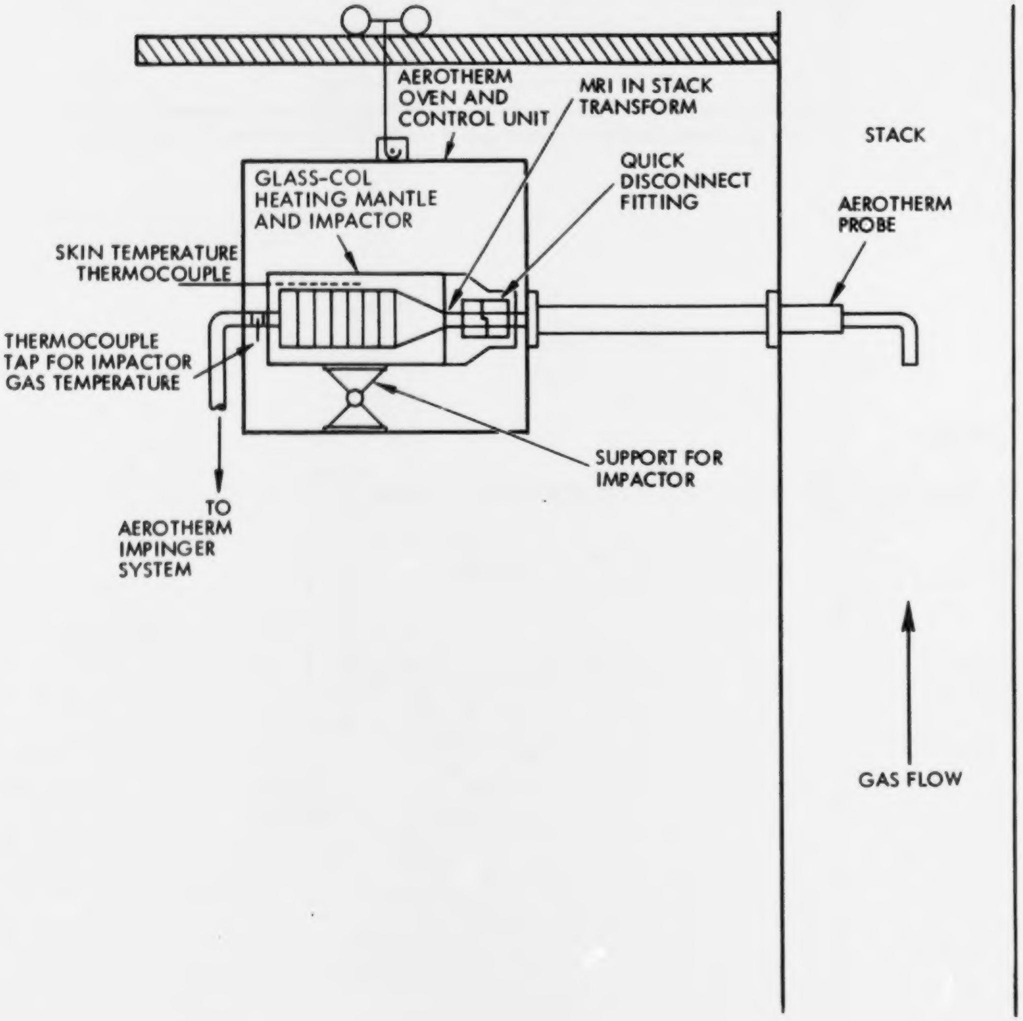

AEROTHERM OVEN AND CONTROL UNIT
MRI IN STACK TRANSFORM
STACK
QUICK DISCONNECT FITTING
GLASS-COL HEATING MANTLE AND IMPACTOR
AEROTHERM PROBE
SKIN TEMPERATURE THERMOCOUPLE
THERMOCOUPLE TAP FOR IMPACTOR GAS TEMPERATURE
SUPPORT FOR IMPACTOR
TO AEROTHERM IMPINGER SYSTEM
GAS FLOW

Figure 2. MRI Impactor Set-Up

H_2SO_4 Sampling--

The development of this method grew out of a basic gap in measurement methodology for H_2SO_4 in particle-laden gas streams. Currently there are two EPA compliance methods for SO_x measurements. In both EPA Method 6 and Method 8, the H_2SO_4 is separated from SO_2 by passing the gas stream through an impinger of 80% isopropanol (IPA) followed by two impingers of 3% H_2O_2. The IPA collects the H_2SO_4 and passes the SO_2 into the H_2O_2 impingers where it is oxidized and collected as H_2SO_4. While these methods are the EPA compliance methods, problems have been found in trying to measure H_2SO_4 in particle-laden streams using these systems. In both procedures inefficient particle removal prior to the first impinger leads to variable positive interferences from sulfate containing fly ash, and catalytic oxidation of SO_2 in the IPA impinger. The precision of Method 8 has been studied, and it was shown to be in excess of ± 50%. Because of these problems, an alternate H_2SO_4 method is needed.

The controlled condensation procedure for collecting H_2SO_4 is a likely candidate because of its simplicity and clean separation of particulate matter, SO_2, and H_2SO_4. This procedure is based on the separation of H_2SO_4 from SO_2 by cooling the gas stream below the dew point of H_2SO_4 but above the H_2O dew point. Cooling is accomplished in a water-jacketed coil (Figure 3) where the H_2SO_4 is collected. Any aerosol not collected in the coil is collected on the glass frit. Particulate matter is removed from the gas stream prior to reaching the cooling coil by means of a heated quartz filter placed after the heated glass probe and before the condensation coil. While the basic idea of a controlled condensation to separate SO_3 from SO_2 had merit, the system design and operating parameters had several built-in difficulties. Consequently, a laboratory study (Task 13) was initiated by TRW to optimize:

- Probe, filter, and coil heating temperature
- Particulate removal system
- Filter selection

The result was a method capable of measuring H_2SO_4 with a laboratory precision of ± 7%, using an improved filtration system and an inert filter material.

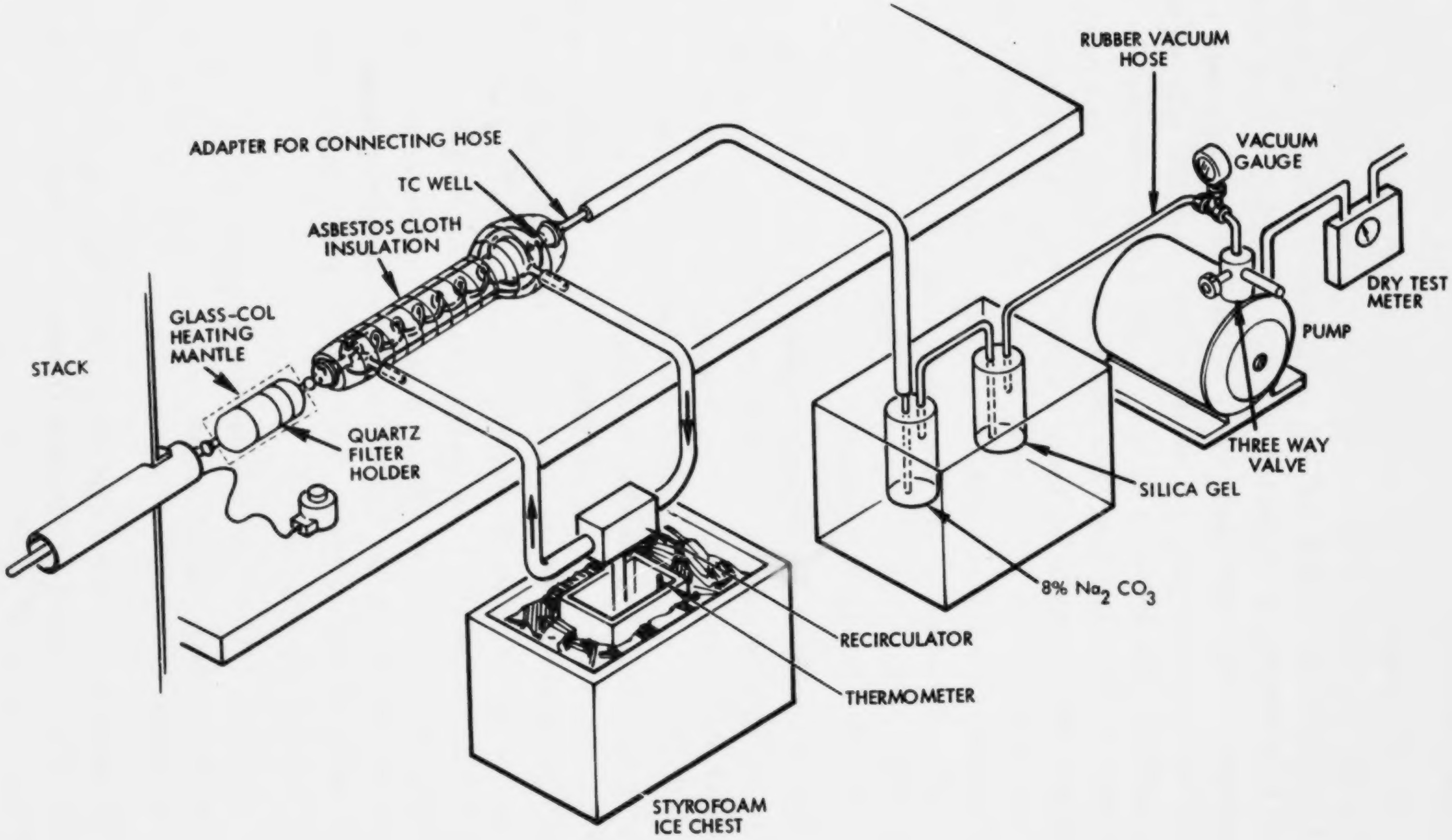


Figure 3. Controlled Condensation System Set-Up

Quality Assurance--

The quality assurance activities under this task were devoted to document procedures and on-site assistance and training. In the procedures document describing the aerosol sizing and SO_3 sampling procedures, information was provided on:

- Equipment care and usage
- Guidelines for laboratory techniques
- Specific critical area checklists for each procedure
- Data interpretation aids to monitor the quality of the results achieved
- Specific maintenance and calibration schedules
- Troubleshooting and repair schemes.

In addition to this documented quality assurance activity, an on-site training session was given to train the TVA personnel on the use of all the equipment and procedures. Throughout the program senior TRW personnel were available for consultation over the phone or for troubleshooting in the field.

2.2.4 Summary of Results and Recommendations

As a result of this program, procedures for aerodynamic sampling at the inlet and outlet of an FGD were developed and used at the Shawnee FGD Test Facility. Using these procedures, Bechtel and TVA personnel studied the mass percent penetration for the TCA and Venturi scrubber systems at Shawnee.

As a result of this task, several areas of continuing or new work are possible. It is recommended that:

- Continued on-site and verbal assistance be provided to the Shawnee Test Facility in the area of trace element sampling and analysis.
- Support be given to improved process measurement at the FGD units.
- New control strategies be developed based on improved process measurement of such species as $SO_4^=$, $SO_3^=$, Ca^{+2}, and Mg^{+2}.

2.3 TASK 3 SUPPORT TO OCEAN INCINERATION

2.3.1 Objective

Disposal of chemical waste products in the United States has long been accomplished via landfill and ocean dumping and more recently by thermal destruction in land-based incinerators. Under EPA contract 68-01-2966, TRW has been involved in a program to evaluate the destruction efficiency of various land-based incinerator types matched with specific waste products. Sampling and analysis strategies were patterned somewhat after EPA methodology and philosophy. However, the EPA manual "IERL-RTP Procedures Manual: Level 1 Environmental Assessment" was still in preparation and not issued at that time.

Land-based incinerators must be equipped with costly effluent control or recovery systems for removal of HCl from the combustion gas stream for disposal of chlorinated organic waste products, one of the major organic chemical waste categories. This by-product then becomes a secondary disposal cost. In contrast, incineration at sea does not require the HCl recovery system. A remote ocean area, judiciously chosen, avoids the problems of acid damage to population, vegetation and structures. The ocean is a very large, slightly alkaline "scrubber" for neutralization of the HCl, and the decrease in pH or increase in chloride content is imperceptible.

In 1974, the EPA granted the first research permit for ocean incineration of chlorinated organic waste to the Shell Chemical Co., and test burns were performed in the Gulf of Mexico that same year. Preliminary evaluation of these tests, as reported in EPA Report #EPA-430/9-75-014, together with test programs conducted in Europe by the Dutch, French, and Germans, indicated that ocean incineration can be a viable; cost-effective alternative to other disposal methods if adequate process control regulations can be promulgated for protection of the environment.

The technical objectives of this task, therefore, were to:

- Evaluate at-sea incineration processes for the destruction of chemical waste products, especially chlorinated organic materials, on board the Matthias III and M/T Vulcanus incinerator vessels.
- Develop guidelines for incinerator design, operational controls, monitoring methodology and acceptance criteria to be utilized by EPA and IMCO in establishing at-sea incineration permit requirements.

2.3.2 Technical Approach

The objectives are summarized in this series of subtasks having the following technical requirements:

- Observe second test burn of organochloride waste aboard the Matthias III incineration ship.
- Evaluate and report on incinerator operation, controls and waste destruction efficiency.
- Analyze feed waste samples for C, H, N, S, and Cl to support combustion efficiency evaluation.
- Determine effect of incineration on surrounding waters by analysis for total organic content (TOC) and chlorinated organic content.
- Acquire and perform statistical analysis of existing thermal data to correlate wall temperatures with flame temperatures.
- Issue detailed reports on observations, analyses, calculations, conclusions, and recommendations.
- Prepare a guidelines document for EPA to use in support of the IMCO intersessional work group which is developing regulatory and technical requirements on incineration at sea.

2.3.3 Results

Matthias III Test Burn--

The first Matthias III test burn was witnessed in June 1976 by TRW on EPA Contract 68-01-2966, and a report was issued indicating technical problems existed which precluded granting of an EPA permit for burning U.S. wastes. This report (1) contains necessary background information on the design and operation of the Matthias III incinerator and the testing performed by the French. Subsequently, we were directed under this task to witness a second test burn aboard the Matthias III in the

North Sea in August 1976. EPA was notified that operating and/or design modifications to correct the problems identified in Reference 1 had been completed. The purpose of the second trip was to observe the performance of the incinerator ship, determine compliance with EPA operational requirements, observe a preliminary burn of solid waste and acquire and analyze seawater samples upstream and downstream of the ship during the burn. Two liquid waste samples were also taken during the test burn and anlyzed by TRW. The results are delineated in Table 2. A variety of drummed solid wastes were also incinerated using the solids inlet port and rotating table system in the furnace.

During this burn, equipment was installed and operated by Drägerwerk AG to monitor CO, CO_2, O_2 and chlorinated organic emissions. The last instrument apparently malfunctioned and was not operating during the test. The following equation was used to compute combustion efficiency:

$$N = \left(\frac{C_{co_2} - C_{co}}{C_{co_2}}\right) \quad X\ 100$$

A thorough, detailed report was issued for the second test burn including tabulated CO_2, CO, O_2 and run data, entitled "Status of Ocean Incineration of Organic Chlorides Aboard Matthias III as of 3 September 1976". The conclusions of that report are highlighted here.

The Matthias III has shown a striking improvement in the combustion of organic chloride wastes as compared to the burn of 5/31-6/3/76. Combustion efficiency values considerably better than 99 percent have been demonstrated throughout the present burn. The plume was consistently white in color and the flame zone was maintained within the incinerator stack.

Temperature measurements indicated the flame temperature in the incinerator to be consistently above 1200°C, and to lie between 1240°C and 1420°C. Wall temperature measurement was shown to be a predictor of flame temperature.

TABLE 2. RESULTS OF WASTE ANALYSIS

Sample	Carbon Wt. Percent	Hydrogen Wt. Percent	Nitrogen Wt. Percent	Halogens as Chlorine Wt. Percent	Sulfur Wt. Percent	Oxygen and Other[a]	Specific Gravity at 25°C	Thermal Content Kcal/Kg
F/M/W-1	43.8	5.3	1.6	40.9	0.2	8.2	1.179	5240
F/M/W-2	41.9	5.5	1.6	38.2	0.3	12.5	1.171	4960

[a] By difference

Seawater analysis for pH, total organic carbon and total chlorinated organic matter revealed no detectable difference between upwind and downwind samples.

The EPA requirements for incineration of organochlorides at sea have been met, in general, with the exception that warning and automatic shutdown of the process upon a temperature fall below 1200°C have not yet been incorporated into the system. However, data and thermocouple locations for warning and shutdown at furnace temperatures of 1300°C and 1200°C, respectively, have been determined.

The improvement in combustion efficiency appears to have been achieved by increasing the relative amount of combustion air. This effect was brought about by reducing the waste throughput by approximately a factor of two.

Analysis of M/T Vulcanus Incinerator Temperature Data--

The EPA Operational Requirements (1, 2) for ocean incineration of organic chlorides include a requirement for emergency waste shutoff if the temperature should drop below 1200°C in the incinerator. A statistical analysis of data obtained during operation of the Vulcanus was made. The detailed results were sent to the Task Officer in a separate letter report.

The report gave the following conclusions:

- Correlation is poor between wall (thermocouple) and flame (pyrometer) readings.
- Based on the data available, the wall temperature is not as good a predictor for flame temperature as might be desirable.
- Using the best thermocouple data (controller, rear furnace) a reading of 1062°C at the wall could be used to sound a warning for 1300°C in the furnace, with a 0.80 probability.
- Similarly, a reading of 985°C would predict a front furnace temperature of 1200°C with a 0.975 probability.

If additional data could be made available, better statistical predictions could probably be made. Approximately 40 data points (both wall and flame) at two- or four-hour intervals would be useful. The methods of statistical analysis are the same as those used on the similar Matthias III data. These methods are described in Reference 2. The data on which the statistical analysis is based are taken from Table V-4, "Disposal of Organochlorine Wastes by Incineration at Sea," EPA-430/9-75-014, dated July 1975, pages 35, 36 and 37.

Additional operational, performance and emissions data were obtained by the TRW sampling team aboard the Vulcanus during burning of Shell Chemical Co. chlorinated organic wastes in March 1977 under EPA Contract 68-01-2966 (Reference 3).

Guidelines for Intersessional Work Group on Incineration at Sea--

The purpose of this subtask was to assist EPA in generating technical considerations and guidelines to be utilized in international agreements on control of incineration at sea. EPA would subsequently submit these recommendations to the IMCO Intersessional Working Group for Incineration at Sea at their London, England meeting. It was also planned to employ these guidelines to establish U.S. regulations.

Reference 4 is the document resulting from this subtask effort and is entitled "Rationale for Annex A to Suggested Special Provisions for Control of Incineration at Sea". The report describes the "rationale", i.e., the technical justification and methodology, for Annex A requirements on:

- Section II — Test Methods of Characterize Waste
- Section III — Guidelines for Incinerator Operations and Monitoring
- Section V — Procedures to Determine Harmlessness of Stack Emission Products

Special acknowledgement is given here to the many contributions, suggestions and general help provided by Dr. Ron Venezia, the Task Officer at IERL and Mr. Russ Wyer, Deputy Director of the Oil and Special Materials Control Division.

Trips and Special Coordination--

By the nature of the work content and deliverables under this task, extensive travel to meetings and the test sites and coordination with the incinerator ship operators, government and private agencies, etc., were required. Three meetings at RTP with the IERL Task Manager and three meetings at Washington with the Deputy Director of the Oil and Special Materials Control Division and others were supported to plan the site visit, observation requirements, report format and to develop the regulatory guidelines. A partial list of the firms and agencies interacting on this task are as follows:

- EPA
  - Oil and Special Materials Control Division, Washington, D.C.
  - IERL, RTP
  - Region VI
- U.S. Coast Guard
- French Atomic Energy Commission Cerbom and Ministry of Environment
- Meneba, SBB — Matthias III
- Hansa Lines, Ocean Combustion Services — M/T Vulcanus
- Shell Chemical Company
- French Ministry

Advisory groups participating in one of the Washington meetings on IMCO guidelines included U.S. Depts. of Commerce, Interior and Labor, the U.S. Coast Guard, the Naval Research Laboratory, Shell Chemical Co. and several public environmental groups.

2.3.4 Summary of Results and Recommendations

The accomplishments of this task have a valuable contribution to the continuing development of efficient and safe disposal of hazardous organic wastes by means of at-sea incineration. The work reported in this task was an important facet of the overall EPA effort to establish:

- Minimum flame temperature at 1200°C for complete destruction
- The correlation of wall temperature as measured by a thermocouple with flame temperature as measured by an optical pyrometer
- Fuel and combustion air feed rates
- Automatic emergency shutoff requirements

- Use of on-board equipment to monitor destruction efficiency based on CO and CO_2 measurements
- A U.S. EPA policy in support of international regulations to be issued by IMCO.

Most recently, the technology developed by TRW under EPA sponsorship for process control, monitoring, sampling and analysis was successfully employed in meeting EPA Permit Requirements for the safe destruction of 11,000 metric tons of Herbicide Orange containing the hazardous trace compounds, TCDD on board the M/T Vulcanus. It is anticipated that this activity will lead to many similar benefits in the future.

2.4 TASK 5 SASS TRAIN LEVEL 1 CHECKOUT

2.4.1 Objective

This task, which was one of the earliest in the TLE project, had two separate though related objectives. One was to use and evaluate one of the first SASS trains produced, both in general terms and specifically, in regards to its use during the testing conducted on board the incinerator ship M/T Vulcanus in the Gulf of Mexico. The second objective was to use the samples collected in the SASS train evaluation portion of the task to test and evaluate the recently published Level 1 analytical procedures.

2.4.2 Approach

The SASS testing was conducted on a 10 million Btu, TRW Low-NO_x burner fired with No. 6 residual oil. The SASS was operated in the configuration to be used for the shipboard tests which was: 15' water-cooled probe, 50' of heat-traced sample line, no cyclones, filter, XAD-2 module, and impingers. The probe was positioned in the combustion chamber of the burner and the train was operated at temperature for several consecutive days and two sets of 30 m^3 samples were collected.

These samples were analyzed following the IERL-RTP Level 1 procedures manual. The complete organic scheme was tested including C7-C12 GC, LC, Grav/IR, and LRMS. SSMS and analyses for Hg, As, and Sb were also performed. Work on this task was initiated in June 1976 and completed in November 1976.

2.4.3 Technical Discussion

The key element to understanding the contribution of this task is timing. When this task was begun, there were only three SASS trains in existence and the IERL-RTP Level 1 manual had been first published in the same month. Several contractors were scheduled to begin implementing the SASS and the Level 1 procedures and a preliminary assessment of potential problem areas was desired.

Many of the problems identified in Task 5 were addressed very quickly, thereby preventing the repetition of errors by several contractors. This was particularly true of the SASS train problems such as poorly sealing impinger caps, difficulties with the inflexible stainless steel connecting tubes for the impingers, and failure of the Teflon o-ring seals. These were relayed to Aerotherm/Accurex and appropriate changes were implemented by them for subsequent SASS trains.

Work was also performed on this task to address serious inorganic analytical problems with the Hg, As, and Sb methods. In each analysis, procedural and matrix problems were encountered that impaired the quality of data that could be produced. By analyzing numerous blanks and spiked controls for each Level 1 sample matrix, modifications to the methods were developed that met the Level 1 accuracy (± 2 to 3 factor) requirements.

2.4.4 Summary of Results and Recommendations

The scope of this task did not include providing solutions to all of the identified problems. Wherever possible solutions were offered, however, other problems (e.g., stainless steel component contamination in the Parr bomb procedure) became the subjects of in-depth examination under other tasks and contracts. These solution-oriented studies conducted after the completion of Task 5, eventually lead to refinements of the Level 1 procedures such as the quartz-lined Parr bomb method. Thus the chief result of Task 5 was to identify areas needing further study. These areas have now, at the present time, all been addressed and the resulting recommended Level 1 modifications have been assembled as TRW's input to the Level 1 revisions under Task 5.

2.5 TASK 7 INORGANIC COMPOUND IDENTIFICATION

2.5.1 Objectives

This task was devoted to the study of measurement procedures for inorganic compounds. While this task was broad in its nature, its main goal was to advance the state of the art for identifying specific inorganic compounds in samples of environmental interest. In this task several specific areas were investigated.

- Literature review - references on compound identification for specific elements like As, Se, Sb, Hg, Cd and Zn were compiled.
- X-ray diffraction - determination of the sensitivity of specific compounds in an environmental matrix.
- Infrared analysis - compilation of literature sources and comparison of conventional IR and FTIR.
- Selective reduction of As^{+3}/As^{+5} - a chemical approach to the selective reduction of As^{+3}/As^{+5} in aqueous environmental samples was investigated.
- Mass thermal analysis - studies were initiated to determine if volatile inorganic compounds could be thermally desorbed from the surface of collected particulate matter.

In addition to these specific areas of research conducted under this task, TRW has supported EPA/IERL programs in the area of advanced inorganic analysis. In this role TRW was charged with design, testing and application of advanced analysis schemes for the determination of compounds from process streams including FBC bed materials and combustion source emission streams. As an end result TRW developed a comprehensive inorganic compound identification scheme, which was detailed in a procedures manual for Level 2 inorganic sampling and analysis.

2.5.2 Approach

In these sections the approach taken in each of the technical areas investigated will be discussed.

Literature Survey--

An extensive literature investigation was conducted to survey available sampling and analytical methodologies for inorganic compounds in solid, liquid, and gaseous streams with particular emphasis on instrumental methods (e.g., XRD, IR, RAMAN, XRD, SEM-EDX, SIMS ESCA, etc.). Efforts were made to develop information for each method on minimum quantity of detectable material, minimum sample size required for analysis, precision and accuracy of the method, costs, and commercial availability.

A literature search was conducted for the years 1970-1976 for the journals Analytical Chemistry and Environmental Science and Technology. Pertinent articles from these journals were obtained and the majority were filed by type of analytical method used. Emphasis was given to the Analytical Chemistry Reviews (April 1974, 1975, 1976) which summarize current research conducted on inorganic compounds using each analytical technique. In addition, Air Pollution Abstracts were reviewed (1971-1976); all abstracts were scanned, and the most pertinent articles were abstracted and/or ordered. A similar search was conducted on the NTIS search bibliography NTIS PS-75/527, entitled: "Chemical Analysis of Aerosols and Airborne Particulates."

Search of in-house material was completed and literature not available in-house was ordered. The accumulated file has been further refined to identify the most definitive literature. Key authors and areas of concomitant interest have been tabulated. Telephone contacts were conducted. As part of the on-going efforts, information was utilized on computer searches. These include Lockheed DIALOG Information Retrieval Service for Chemical Abstracts, Scisearch and NTIS data bases; SDC Search Service Data Bases for Pollution abstracts.

The literature (journal articles, reports and books) obtained were filed by analytical method to provide continuing back-up and state of the art information to this task.

X-Ray Diffraction--

In this subtask work was conducted in three areas:

- Sensitivity studies of pure compounds in a matrix similar to combustion source samples.
- Sample handling procedures for mounting and analysis of samples.
- Analysis of actual combustion source samples to study the practical application of XRD analysis.

In the first phase pure compounds were mixed with a suitable dilutant to simulate the environmental matrix. This work was to provide baseline sensitivity data from an experimental standpoint. Since mounting procedures can appreciably affect the results of an XRD, a standardized approach was developed to optimize test conditions. The end result was a study of actual samples of fly ash, FBC bed material and coal char.

Infrared Analysis --

Infrared analysis provides a useful screening method to indicate the presence of specific anions or even compounds. The work conducted in this subtask consisted of:

- Compiling reference IR tables for inorganic materials in the mid and far IR.
- Selection and testing of candidate mounting mediums (mulls vs pellets).
- Comparison of FTIR and IR scans.

Selective Reduction of As^{+3}/As^{+5} --

The goal of this subtask was to analyze process streams, stack gas samples and solid particulate specifically for inorganic As^{+3} and As^{+5}. Chemical speciation of inorganic As^{+3} and As^{+5} provided:

- Information on the true toxicity of the sample.
- Back-up information if As_2O_3 and As_2O_5 cannot be seen by XRD.
- A means for analyzing for As^{+3} and As^{+5} that passes through SASS train particulate collection system.

A method based on the selective reduction of inorganic As^{+3} and As^{+5} (Reference 5) was evaluated. The solution containing As^{+3} and As^{+5} was buffered at specific pH's (1.5 and 4.5) and reducing agencts ($NaCNBH_3$ and $NaBH_4$) are added. The evolved AsH_3 was captured via a cold trap and organic solvent and could be analyzed by either flameless ASS, GC/ECD, or D.C. discharge. The method as developed by Bramen (5) used a one-of-a-kind D.C. discharge system to quantitate the amount of AsH_3. This subtask verified Bramen's work and attempted to extend it to conventional AAS analysis.

Mass Thermal Analysis--

Attempts to determine the type and quantity of volatile inorganic compounds present in samples was made by monitoring the weight loss and identifying the gas products using a TGA/MS analysis. TGA/MS is particularly suited to the identification of volatile components and within the limits of the temperature program should be able to identify materials by their degradation products.

Initial tests were conducted with a DuPont 951 TGA using:

- Pure compounds
- Pure compounds mixed with coal fly ash.

If these tests were successful, design and fabrication of a TGA/MS interface was to be initiated.

Special Studies--

As the task continued, interesting and potentially useful methods and procedures were cursorily studied. To date this task has looked at:

- The use of Proton Induced X-Ray Emission (PIXE) as an accurate multielement analysis.
- SEM-EDX analysis of environmental samples.

2.5.3 Technical Discussion

The following paragraphs will discuss the major accomplishments in each of the areas of research.

Literature Survey--

The literature survey conducted under this task compiled over 300 journal articles organized into a wide range of topics. In addition to this literature, computor searches for analysis methods using the elements: arsenic, barium, beryllium, boron, cadmium, chlorine, copper, fluoride, lead, manganese, mercury, nickel, selenium, tin, vanadium, and zinc were completed.

X-ray Diffration Studies--

X-ray diffraction technique is a relatively simple analytical tool widely used for qualitative and quantiative identification of various crystalline compounds present in a amorphous matrix. However, the sensitivity of the X-ray diffraction method is inferior to other methods, and the sensitivity may vary depending on the compound under study and the matrix.

The main goal for X-ray diffraction studies performed at TRW during this task was to investigate the analytical capability of a typical commercial X-ray diffractometer (in this case a GE XRD-5) to detect small amounts (1-10%) of various materials of environmental interest.

Sample Handling Procedure -- The handling of environmental samples imposes two major difficulties; first, small amounts of pure compounds are usually mixed with an amorphous matrix and, secondly, the material can be impacted on glass fiber filter which produces a background scattering which can mask the diffraction pattern due to crystalline species. Two approaches: removal of the actual sample from the filter, and sample preparation to ensure the highest possible intensity were studied.

To simulate an environmental matrix, two candidates, silicic acid ($SiO_2 . x H_2O$) and ground glass were tested for use on an amorphous filler for the laboratory samples. Both produced an amorphous background, but silicic acid was easier to disperse. The sample preparation procedure was:

1) The pure chemical compound, as well as silicic acid were ground to achieve <40μm size.

2) The test compound and silicic acid were weighed and premixed in a test tube. Then a mixture of collodion with reagent grade ethanol in a 1:4 ratio was used as a suspension medium in which the samples were mixed ultrasonically for 10 minutes. The 1:4 ratio of collodion and ethanol, as well as dispersion time were found experimentally simply by trial error and were kept constant during this series of experiments. After 10 minutes of dispersion, the medium looked very uniform.

3) Using a pipet, the dispersed sample was spread over the glass slide, on which the illumination area was framed using masking tape. After ∿10 minutes of drying in air, the sample was ready to run on XRD-5.

All laboratory samples (compound and silicic acid) and actual samples tested were mounted on the glass slides in this fashion. In some cases the material was impacted on a glass fiber filter and could not be easily removed. In this case alternate methods such as using Scotch tape to remove the particulate matter or direct analysis of the filter with the particulate matter on it were tried. As it turned out, both of these alternate methods did not provide as good results as the mechanical agitation of the filter and collodion mounting of the material removed. The reason for that seems to be due to a low pick up of sample by the Scotch tape (∿20 mg), or, in case of the filter mounted on a glass slide, the high background due to amorphous scattering of the filter.

It should be mentioned, however, that the proposed sample preparation technique in each particular case must be applied with care. The wetting and drying properties of a particular environmental sample could differ significantly, as it did in the case of studying filter and cyclone catch from an Aerotherm HVSS, as well as the samples from the mechanical and electrical precipitator of the Shawnee Test facility. In each case the amount of collodion to disperse the sample was found to be different, and it is believed that the right ratio of collodion and ethanol must be found by trial and error. Another difficulty was the formation of cracks during sample drying; this was most pronounced in the case of filter catch. In these cases, it is recommended that the collodion suspension be spread over a piece of double-sided Scotch tape mounted on the glass slide. This technique prevented cracking in most cases.

Sensitivity Studies of Pure Compounds in an Amorphous Matrix-- As real-life samples usually consist of mixtures of various sulfates and oxides imbedded in amorphous matrix, the sensitivity studies were undertaken with the laboratory samples containing pure compounds mixed with an amorphous filler. The total weight of the laboratory sample was chosen to be 100 mg, which is the approximate amount of material that would be available for analysis. The 100 mg samples were mounted on a glass slide, and run on XRD-5 diffractometer in the 2θ-range around the major diffraction peak.

An inspection of XRD data shows that the most intense diffraction peaks of sulfates and oxides are located at relatively low ($\sim 20^{o}-30^{o}$) diffraction angles, where due to divergence of the X-ray beam, the sample's illumination area is maximized.

The experimental conditions listed in Table 3 were kept constant during this series of measurements. The compounds studied at TRW, their weight fraction in amorphous matrix, as well as the estimated detection limits are tabulated in Table 4. According to the X-ray scattering ability of each compound, the qualitative classification has been suggested.

It should be noted that detection limits of the compounds listed in Table 3 would be significantly lower if more sophisticated equipment was used rather than the XRD-5 diffractometer. Limits of detection for state of the art equipment approaches 0.05% for many compounds.

TABLE 3. EXPERIMENTAL CONDITIONS

Variable	Conditions Employed
Radiation	$Cu_{K\alpha}$
Filter	Ni
High voltage	40 kv
Current	20 ma
Sample's irradiated area	15 x 35 mm
Counting rate	500 c.p.s.
Time constant	1-2 second
Detector	Proportional
Detector's slit	0.2^{o}
2θ scanning speed	2 degree/minute

TABLE 4. XRD DETECTION LIMITS OF INORGANIC COMPOUNDS OF ENVIRONMENTAL INTEREST

Compound	Weight Fraction in Sample	Intensity (c.p.s.)	Estimated Detection Limit (% W/W)	X-ray Scattering Ability
$CaSO_4$	10	700		Strong
	4	250	∿1	
As_2O_3	10	200	2	Intermediate
	2	70		
$HgSO_4$	10	225	∿2	Strong
PbO	10	900	<1	Strong
	1	75		
Cr_2O_3	10	180	3-5%	Weak
MnO_2	2	70	2	Intermediate
SeO_2*	10		∿10	Very broad
$VOSO_4$*	10		∿10	Very broad

*The quality of X-ray spectrum is very poor, mainly due to difficulties with proper dispersion of the sample.

Analysis of the Actual Industrial Samples--

1. FBC Fly Ash (PMB-0085) - The X-ray diffraction pattern of this fly ash, as identified in our study, contained $CaSO_4$ in both the hexagonal and orthorombic forms, but none of the original CaO present in feed material was found. Other compounds, namely $CaAl_2Si_2O_8$ and $KAlO_2$ (or $K_2Al_{24}O_{57}$) were tentatively found.

   Based on standard additional techniques, the 100 mg sample contained ∿20 weight percent $CaSO_4$. The less than ∿10% deviation of the intensity of the SiO_2 line, which ideally should be the same in all three samples, implied that the error in the $CaSO_4$ concentration measurement was not more than 10%.

2. Thermally and Chemically Treated Coal Char - Typically, for all coal char investigated in our laboratory, the X-ray diffraction spectra were obtained in the 2θ of 5° to 50° range. Identification was made on the basis of agreement within ±0.02° of the spacing of the compounds. Because of the overlap of several compounds, unambiguous identification of all the lines was not possible. In particular, it was found that the Na_2CO_3 spectra did not correspond to the literature values and hence, identification of it within the samples was impossible. Tables 5 and 6 summarizes the compounds looked for and whether they were found. Because of the thermal history of the sample, compounds which were normally crystalline could exist in amorphous states, in which case either no spectra or broad band spectra would be obtained. If unambiguous identification was not attainable, the presence of the compound was listed as "possible." A brief description of each sample analyzed is given below.

   a) Original Coal Char — The original char produced only 4 significant lines. These lines can be assigned to either FeC or carbon with a structure similar to graphite. A char assignment based on 2θ values was not possible. The only other potential compound was $Ca_3Fe_2Si_3O_{12}$.

   b) Residue A — Residue A consisted originally of char, $NaCO_3$, CaO, CaF_2 prior to heating and steam treatment. All these components were seen in the sample after heating except for Na_2CO_3. After treatment, the CaO and CaF_2 concentrations appeared to be less. The char components were seen as well as a new compound, CaS. Three compounds

[$Na_2Ca(CO_3)_2$, $Ca_5(SiO_4)_2CO_3$, $CaCO_3$] were possibly identified (Table 5) with $CaCO_3$ being the most probable. Finally the presence of $Ca_{10}Si_{30}O_{15}F_2$ was inferred, but further work would be required to identify it unambiguously.

c) Residue B — This sample originally contained char, K_2CO_3, and CaO. The char lines (FeC or C, and $Ca_3Fe_2Si_3O_{12}$) were present. The presence of CaO was confirmed and appeared to be at a concentration greater than that left in Residue A. The quantity of CaS found was less than was that in Residue A. The presence of $CaSO_4$ was possible (Table 6). A series of compounds [$K_2Ca(CO_3)_2$, Fe_3O_4, $CaSiO_3$, $CaFeSiO_4$, $Ca_5(SiO_4)_2CO_3$] were tentatively identified from their 2θ values, but all were present in the 1-3 percent w/w range or less.

TABLE 5. RESIDUE "A" TENTATIVE IDENTIFICATIONS

2θ	Tentative Identification
26.6	FeC or C
29.2	$Ca_3Fe_2Si_3O_{12}$: $Ca_5(SiO_4)_2CO_3$; $CaCO_3$
33.2	$Ca_3Fe_2Si_3O_{12}$; $Ca_5(SiO_4)_2CO_3$
35.4	Na_2CO_3; $Na_2Ca(CO_3)_2$
43.0	FeC or C; $Na_2Ca(CO_3)_2$; $CaCO_3$

TABLE 6. RESIDUE "B" TENTATIVE IDENTIFICATIONS

2θ	Tentative Identification
25.2	$CaSO_4$(?); $CaSiO_3$
26.6	FeC or C; $CaSiO_3$
29.8	$Ca_3Fe_2Si_3O_{17}$; $CaFeSiO_4$; $CaSiO_3$; $Ca_5(SiO_4)_2CO_3$
33.3	$CaFeSiO_4$; $Ca_5(SiO_4)_2CO_3$
34.0	$CaFeSiO_4$; $Ca_5(SiO_4)_2CO_3$
35.3	CaO_2
43.0	FeC or C
46.5	CaO_2

Infrared Spectroscopy Studies--

Both normal and far infrared are valuable tools in piecing together the composition of a sample. Infrared and Raman spectroscopy were used to analyze and identify lunar rocks during the Apollo program (6). The investigators were able to correlate the fundamental vibrations of $SiO_4^=$ with the bulk composition of the sample. Lunsford (7) used infrared spectrophotometry to determine the chemical form of adsorbed SO_2 on various metal oxides. In the total compound analysis scheme, infrared analysis can potentially identify anions present in the sample and determine the compound containing the anion. The former is fairly easy to accomplish since most anions have characteristic bands that can be used for identification. As Table 7 shows, the region from 1000 to 1500 cm^{-1} should be of great use.

Besides simply identifying the anion, specific correlations are available for individual compounds. Several investigators (8, 9) have done extensive work with inorganic compounds. Tables 8 and 9, respectively, list the characteristic bands for several nitrates and sulfates. Clearly, there are analytical frequencies which can be used to identify compounds, especially if elemental analysis can reduce the number of possibilities.

TABLE 7. USEFUL IR BANDS

Anion	Absorption Bands (cm^{-1})
$SO_4^=$	610 - 690 (m) 180 - 1130 (s)
NO_3^-	610 - 640 (m, sp) 1350 - 1370 (s)
$CO_3^=$	650 - 680 (m) 1430 - 1450 (s)
$SiO_3^=$	∿900 - 1100 (vs)

m = medium, s = strong, sp = sharp, v = very

TABLE 8. INFRARED BANDS OF SOME COMMON NITRATES (CM^{-1})

Compound	Band Category[(a)]				
	VW	W	M	S	VS
$NaNO_3$	2428		836 sp		1358 1790
KNO_3			824 sp		1380 1767
$Ca(NO_3)_2 \cdot XH_2O$	1044		820 sp	$\sim$1430 $\sim$1640	$\sim$1350
$Fe(NO_3)_3 \cdot 9H_2O$			835 sp	1615	1361 $\sim$1785
$Ca(NO_3)_2 \cdot 3H_2O$	2431		836 sp	1587	1378 1790
$Pb(NO_3)_2$		807	726 836 sp		1373

W = Weak, M = Medium, S = Strong, V = Very, SP = Sharp, B = Broad

TABLE 9. INFRARED BANDS OF SOME COMMON SULFATES (CM^{-1})

Compound	Band Category[a]				
	VW	W	M	S	VS
Na_2SO_4		645		620	1110
K_2SO_4					1110 620
$CaSO_4 \cdot 2H_2O$		1010 (sh) 1670	318 2200 (b)	603 667 1630 (sp) 3410 (b)	1130 (vb)
$MnSO_4 \cdot 2H_2O$		510 (vb) 607	660 1025	825 3225 (b)	1135 (vb)
$FeSO_4 \cdot 7H_2O$	990	1150 (sh)	1625	611 (vb) 3330 (b)	1090 (vb)
$CuSO_4$		1020 (sp) 1600 (sh)	680 805 860	1200 ~3300 (b)	1090 (vb)
$PbSO_4$			592 (sp) 623 (sp)		

(a) V = Very, W = Weak, M = Medium, S = Strong, SH = shoulder, B = Broad, SP = sharp

Technical problems that must be addressed include effect and control of moisture content in the sample. The moisture content of the sample will affect the degree of hydration of the compounds present in the sample. It is expected that the samples will have to be dried to a constant water content to simplify the analysis problem. Information from a TGA-DSC analysis will be used to pick a drying temperature that provides water removal without sample decomposition.

In preparing the sample for IR analysis, typically KBr is used as the mulling agent. However, samples that contain reactive materials such as acid sulfates can cause reactions by releasing HBr in a replacement reaction. Aluminum oxide, which is transparent from 2.5 to 15μ, has been tried as an alternate mulling agent, but results have not been good since the fly ash did not stick to the Al_2O_3. Silicon dioxide was also tried (absorption at 1000 to 1100 cm^{-1}) with the same results. Fused SiO_2 works but it is very porous and can pick up contaminants quite easily. The first alternative is to use Nujol or Fluorolube mulls between AgCl plates. This combination minimizes ionic exchange problems as well as crystal deformation that might be caused by the pelleting procedure.

FTIR Results -- During the task, a series of IR spectra were obtained for 5 different fly ash samples. These samples were anlyzed by conventional IR and FTIR in the mid-IR.

The first sample run was Fluidized Bed Combustor material (PMB-0085) supplied by PMB. Figure 4 shows spectra for a 1 mg (A) and 2 mg (B) dried sample placed in a KBr pellet and using a Perkin Elmer 521. Except for the peaks at 600 cm^{-1}, 670 cm^{-1} and 780 cm^{-1}, the spectra was without much detail. Another spectrum (Figure 5) using a mineral oil mull and shown at 5X scale expansion is completely different as now the major band is at 720 cm^{-1} which is not in the mineral oil spectra. While showing reasonable intensity, the spectrum lacks fine detail. This same FBC material was run on a Digalab FTS-14, using scale expansion and computer averaging of 40 scans (Figure 6). The result was a clearly resolved spectra with a wealth of bands shown. Bands associated with $CaSO_4$ are

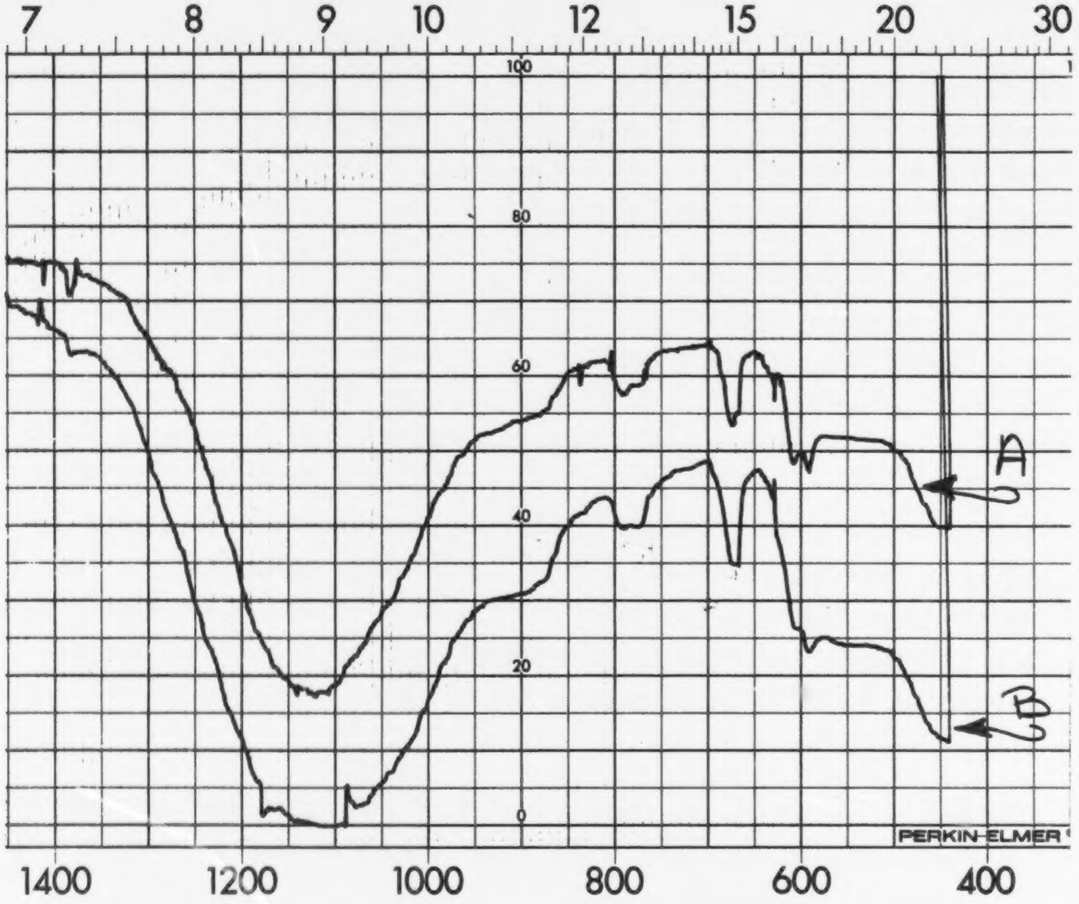


Figure 4. Perkin Elmer KBr Pellet IR Scan of PMB-0085 Flyash
(A)-1 mg, (B)-2 mg

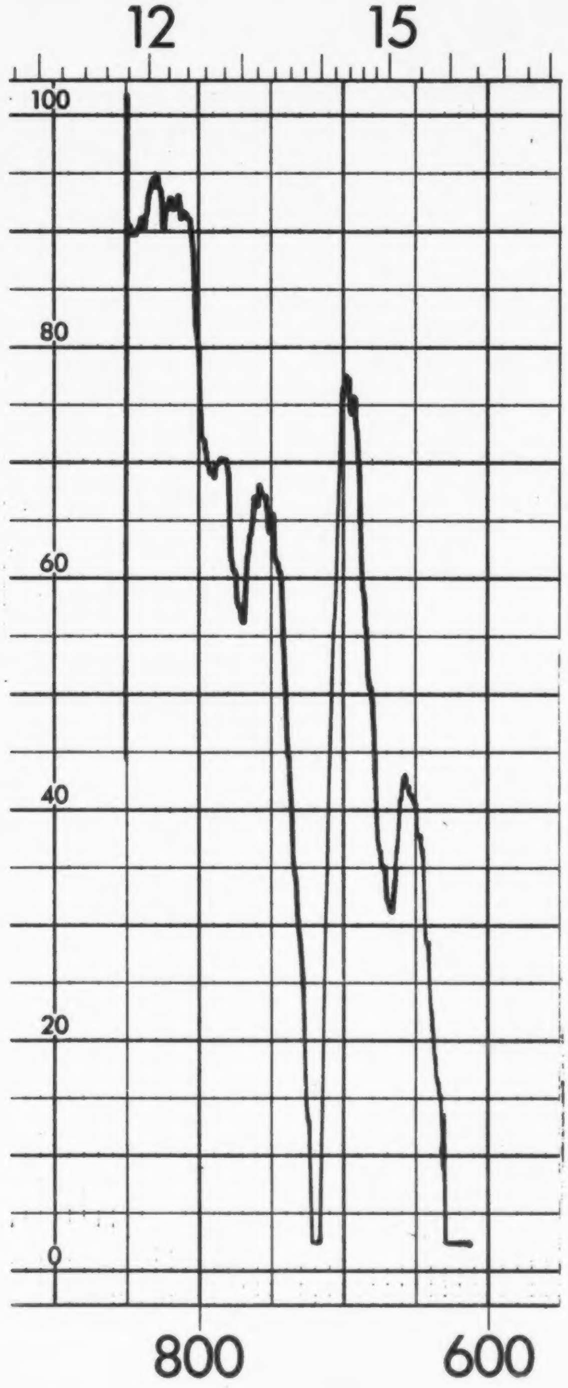


Figure 5. Perkin Elmer 521 IR Scan of PMB-0085
Flyash (5X)

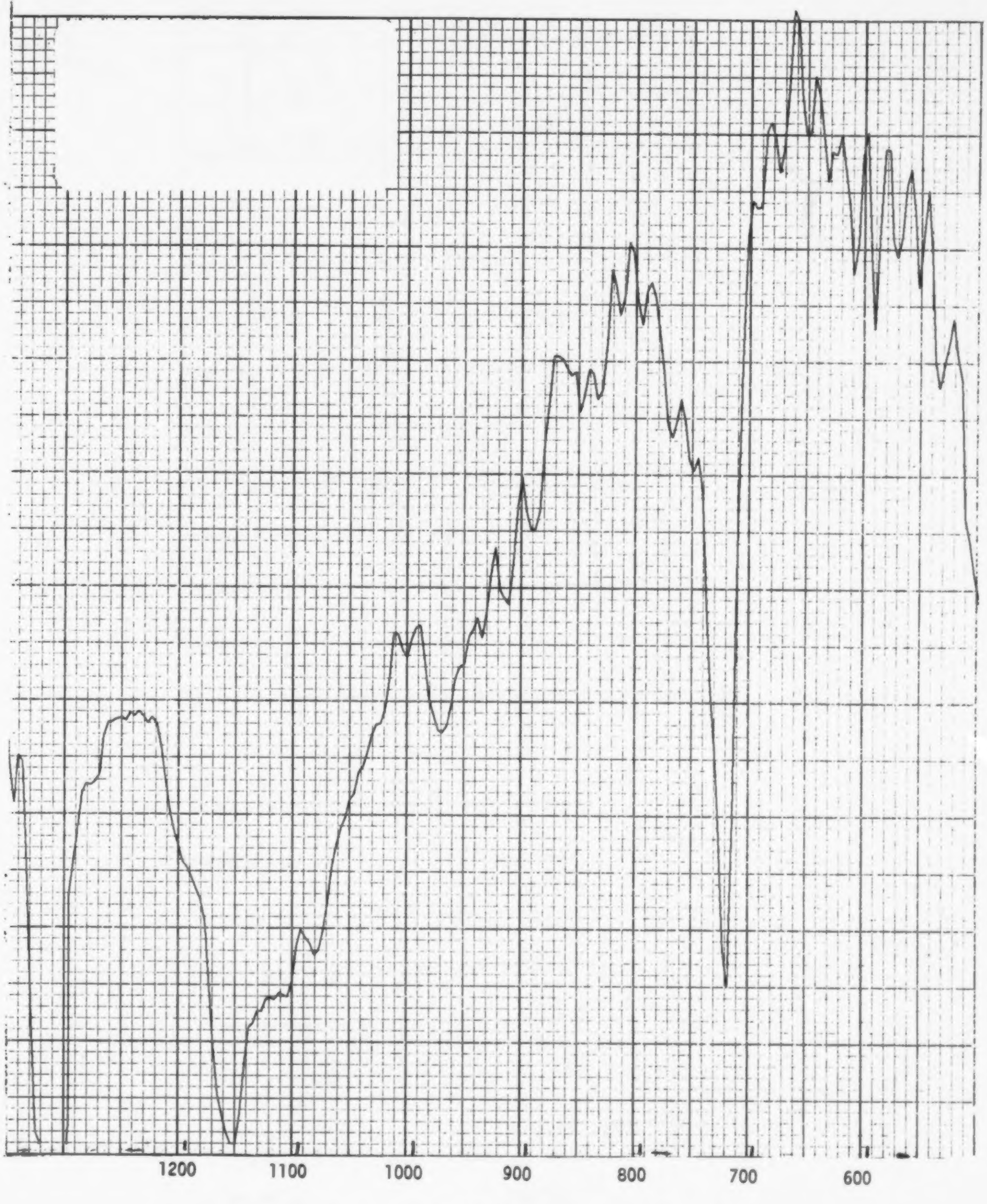


Figure 6. Sample PMB-0085 FBC Flyash

clearly seen at 610 and 670 cm^{-1}. Figures 7 through 10 show a series of samples of flyash taken from the outlet of a coal-fired boiler at the TVA Shawnee Power Plant in Paducah, Kentucky. The particle size essentially decreases in these samples in the order of presentation. Of particular interest is the HVSS filter catch compared to the HVSS cyclone catch. Note the change in peak ratios at 770 and 600 cm^{-1} and the appearance of a strong band at 670 cm^{-1} ($SO_4^=$).

While further work will be needed to identify the bands, the high quality of the spectra and the obvious changes in the position and strengths of various bands shown in the FTIR spectra clearly indicates the utility of FTIR over conventional IR in recognizing changes occurring in the sample. Also,the ability of the FTIR to subtract background spectra can be used to remove unwanted materials. While 40 scans were averaged in this test, 400 or 4000 scans could have been made to improve sensitivity.

As^{+3}/As^{+5} Speciation--

The sensitivity for As^{+3} in the initial experiments was quite low. The low recovery was traced to the effect on pH of the addition of $NaBH_4$ to the sample. The procedure being tested (Reference 5) relies on precise slection of the pH. The hydride of As^{+3} is formed at a pH of 4-5 with $NaBH_4$ while the As^{+5} hydride is formed (after the As^{+3} is removed) at a pH of 1-2 with $NaCNBH_3$ followed by $NaBH_4$. In both cases, the AsH_3 is confined in a LN_2 trap. It was found using Bramen's procedure that the addition of $NaBH_4$ raised the pH in the reaction vessel to ∿9, at which point the hydride generation is inefficient. Additional amounts of KHP were added to offset the alkalinity of the $NaBH_4$. This change resulted in much higher recoveries, but at levels still above an in-house hydride generation scheme based on Zn/HCl. In order to improve the reaction, KI was added to the sample (1 ml 10 percent KI) as a catalyst (10). This change improved the recovery by a factor of 1.8 and was incorporated into the procedure. Based on the background signal, the detection limit was estimated to be 0.04 μg or ∿2 ppb based on a 25 ml sample.

The completeness of the separation of As^{+5} from As^{+3} was studied using samples containing only As^{+5}, but using the As^{+3} reaction chemistry (pH = 4-5, $NaBH_4$). These results showed that when 5 μg of As^{+5} was present, As^{+3} signal of 0.06 μg was found. The presence of KI did not affect these

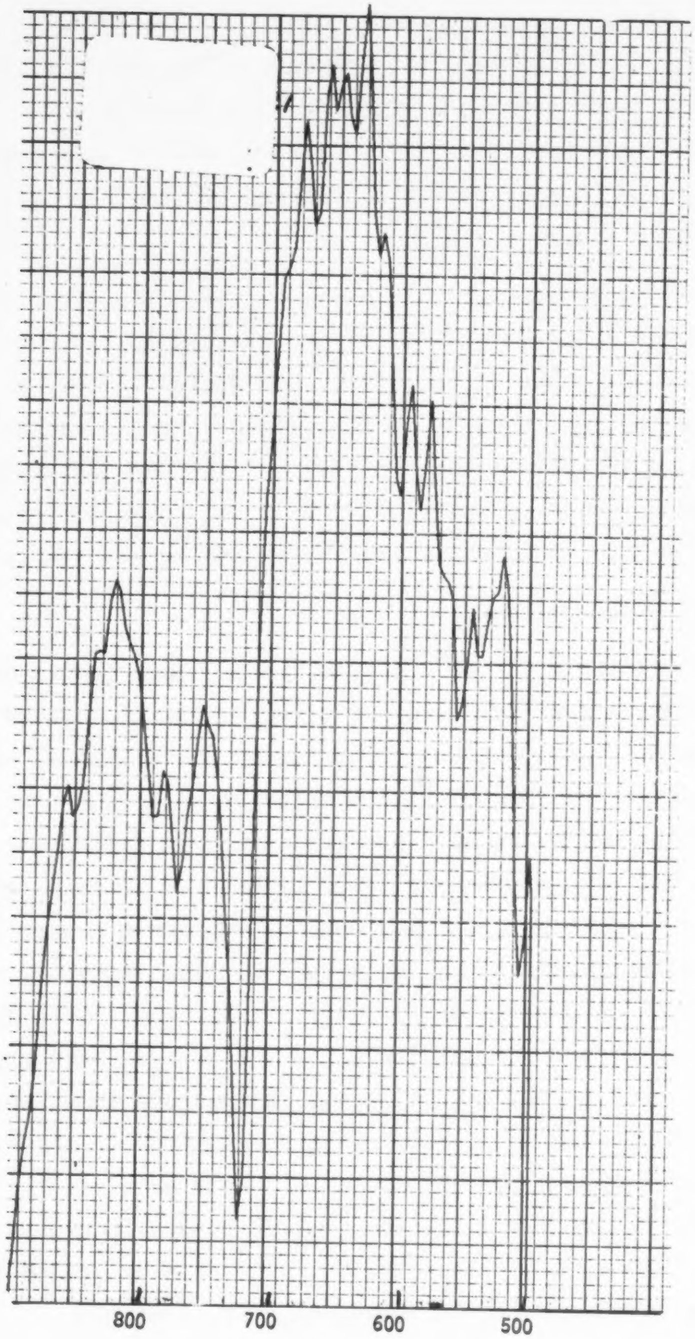


Figure 7. Mechanical Precipitator Flyash Spectrum

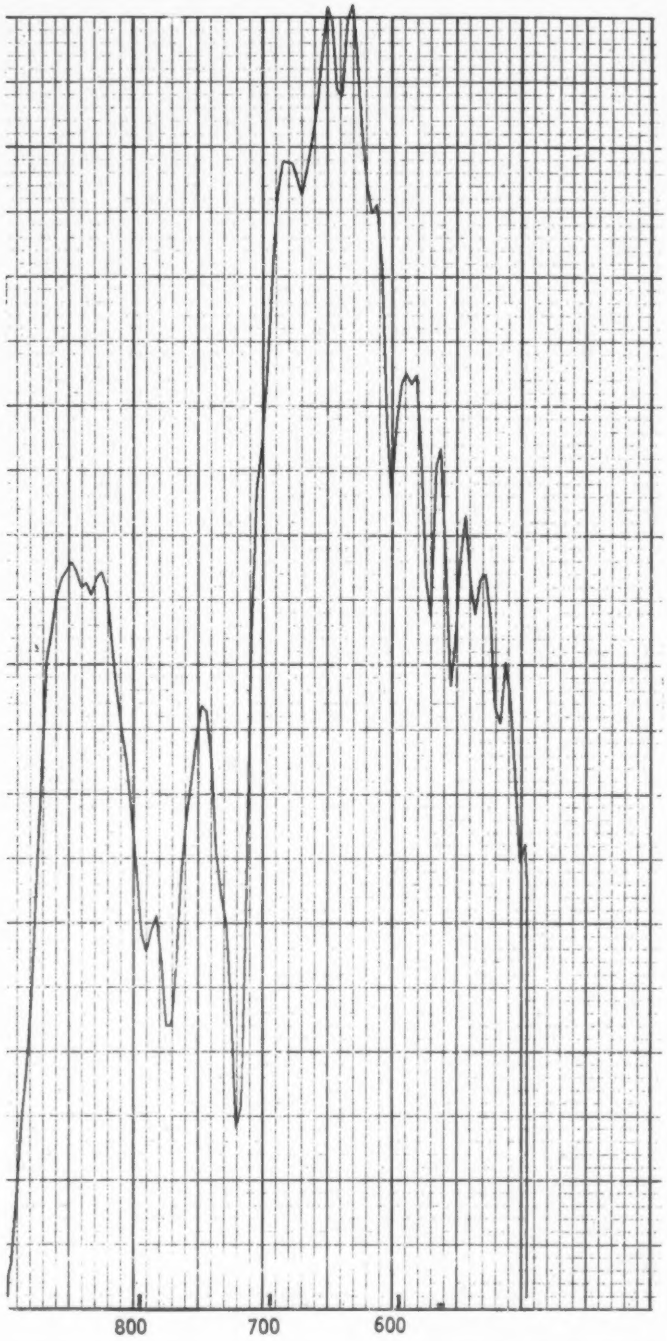


Figure 8. Electrostatic Precipitator Flyash Spectrum

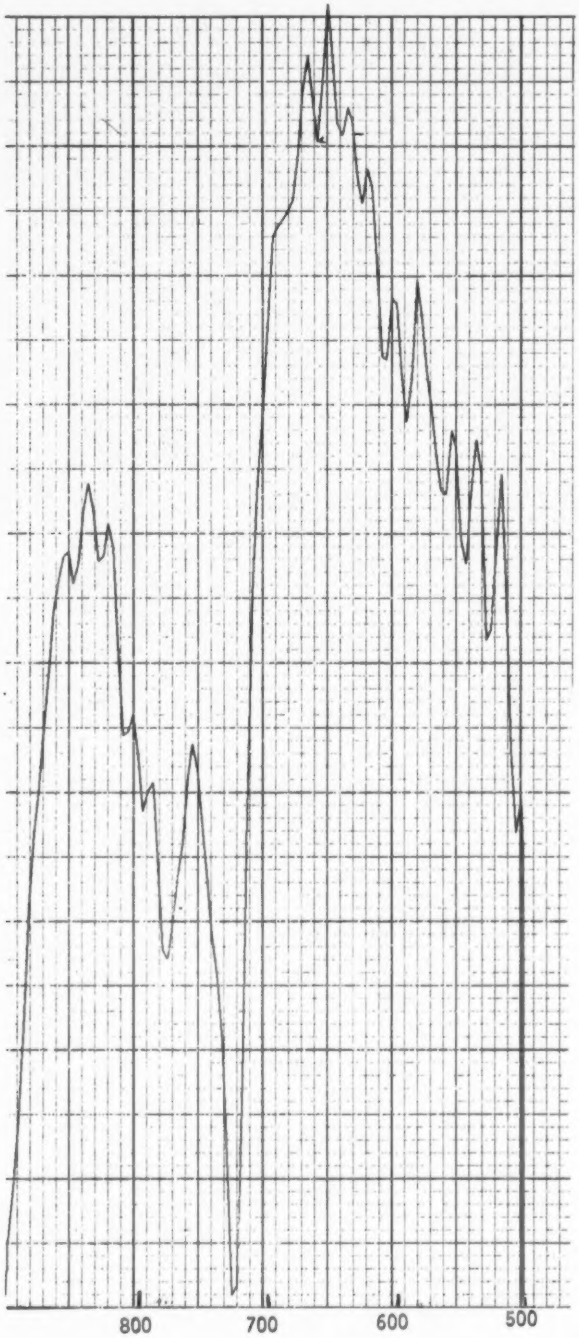


Figure 9. Cyclone From HVSS (INLET) Flyash Spectrum

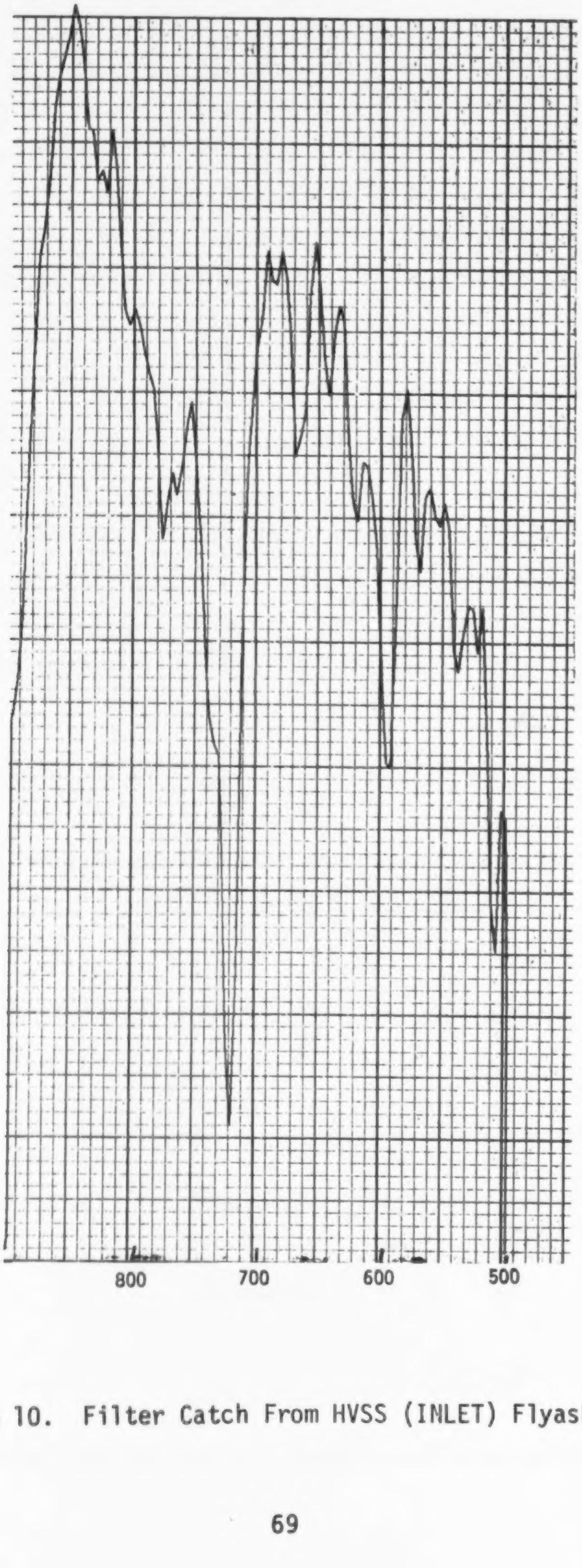


Figure 10. Filter Catch From HVSS (INLET) Flyash Spectrum

results and attempts to oxidize any As^{+3} (As_2O_3) that might be an impurity in the As^{+5} (A_2O_5) produced no noticable drop in signal. Since the recommended operating range of AAS for AsH_3 analysis is 1 µg absolute, appropriate dilutions can be made to minimize the effect of this slight reaction of As^{+5} to As^{+3} hydride formation chemistry. Once these preliminary tests were completed, a calibration curve was run for As^{+3} and As^{+5} using the specific hydride formation chemistry. The results are shown on Figure 11. It was expected that both curves would be identical, since hydride generation occurs from the +3 oxidation state. The difference between the two curves reflects the difference in recovery for the two methods. Since both curves showed good precision (<±10 percent), the reason for the lower As^{+5} recovery was not sought.

Combined samples of As^{+3}/As^{+5} were then analyzed in the same solution to test the coordinated recovery of the procedure. The results are shown in Table 10. While recovery for As^{+3} was reasonable throughout the values tested, the results for As^{+5} were less encouraging. The As^{+5} recovery was depressed further when both reaction chemistry systems were tried on the combined sample.

TABLE 10. AS^{+3}/AS^{+5} SPECIATION TESTS RECOVERY ERROR RESULTS

Input (µg)	Recovered (µg)	Error (%)
As^{+3}/As^{+5}	As^{+3}/As^{+5}	As^{+3}/As^{+5}
5/2.5	4.9/3.0	-2/+20
5/2.5	5.3/3.6	+6/+44
5/2.5	5.2/2.8	+4/+12
	Avg. 5.1/3.1	
1/1	0.68/0.45	-32/-55
1/1	0.80/0.90	-20/-10
1/1	0.80/0.63	-20/-37
	Avg. 0.76/0.66	
0.5/0.5	0.48/0.43	-4/-14

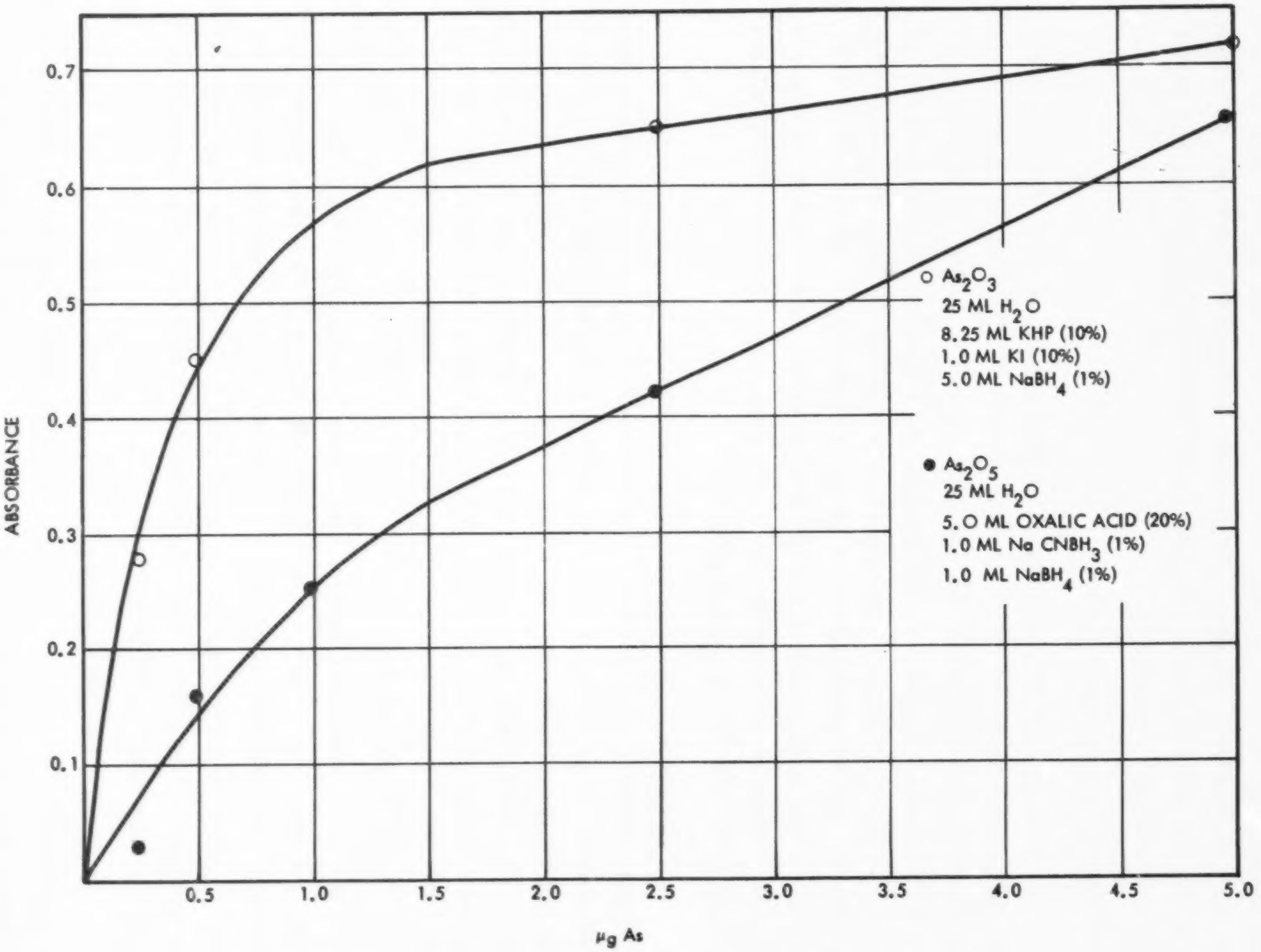


Figure 11. Calibration Curves for As^{+3}/As^{+5}

These results indicate that the As^{+3}/As^{+5} specification using a LN_2 cold trap and AAS is possible. Further work will be necessary to improve the recovery of As^{+5}. The fact that the calibration curves were different for each oxidation indicates that procedural problems were not uncovered by this feasibility study. Further work is necessary to find the cause for this low As^{+5} recovery.

TGA/MS Evaluation Results--

The original objective of this investigation was to determine the feasibility of compound characterization and identification of mating the analytical capabilities of TGA and MS. It was intended to couple the MS directly to the effluent stream of the TGA to permit MS identification of the volatile compounds. However, it was decided to first determine the utility of TGA to characterize a sample of FBC flyash material and then to determine the lowest concentration levels at which a compound in the FBC material could be detected by TGA. The results of these experiments are presented in the following paragraphs.

Two samples of FBC material were run on the TGA (DuPont) under a nitrogen atmosphere employing a 5°C/min heat-up rate and full scale deflection representing ∿13% (w/w) of the sample. The data were reduced and plotted (Figure 12) as percent weight retention versus temperature to permit a direct comparison of the two runs. Although the results of the two runs appear similar, close examination shows that variations between the two runs was as much as 0.5% (w/w) in the temperature range from 200°C to 500°C and greater than 1% (w/w) at 880°C.

TGA scans were next run on three model compounds; $ZnCl_2$, SeO_2 and As_2O_3, to determine their thermal characteristics. The same conditions were employed for the three model compounds as were used for the flyash sample. Each compound was found to display a fairly sharp break in the TGA scan and it appeared that the characteristic break points could be used for compound identification.

Testing of the TGA approach for compound identification was performed by examining mixtures of the flyash and the model compounds. Specifically, mixtures were prepared by adding 1% (w/w) of each of the model compounds to the flyash and TGA scan, then were run. The results obtained for the

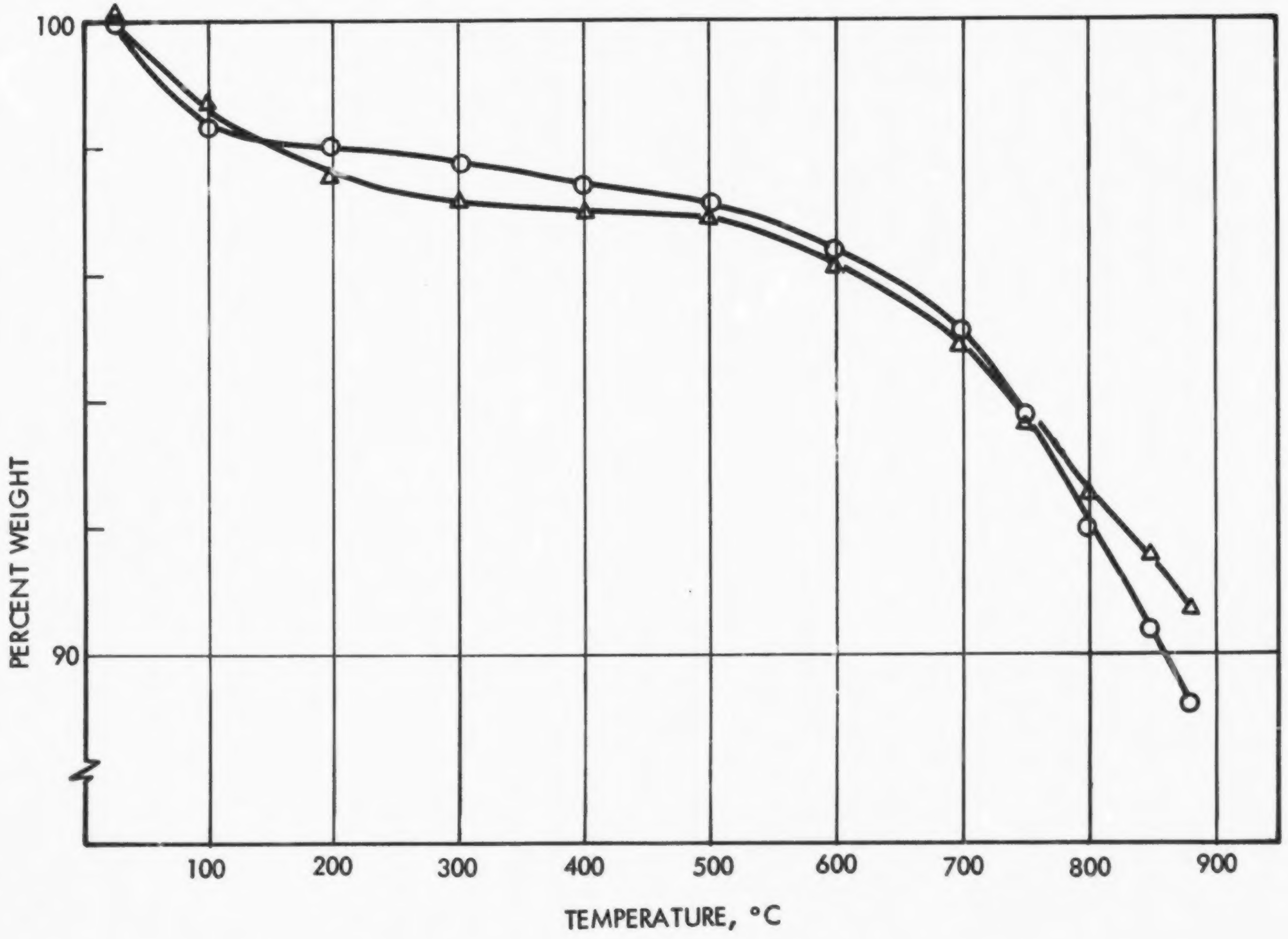


Figure 12. TGA of FBC Material (Nitrogen Atmosphere, $5^{O}C/min$)

three mixtures are presented in Figure 13 together with the TGA scan for flyash by itself. Only the As_2O_3 mixture shows behavior consistent with what would be expected based on the behavior of the pure compounds. A sample of As_2O_3 shows weight loss occurring at 250°C to 300°C. It can be seen in Figure 13 that the As_2O_3 containing sample shows about a 1% difference in weight loss between the flyash and the 1% mixture in this temperature range. However, it is somewhat disturbing that the total weight loss at 800°C is about the same for both samples where it is expected that the mixture should display a 1% greater weight loss. The samples containing the SeO_2 and $ZnCl_2$ failed to show weight losses in the expected temperature ranges of 250°C and 500°C, respectively.

To test this approach further, a flyash sample containing 5% w/w As_2O_3 was prepared and run on the TGA. The results are also presented in Figure 13. It is evident that the 5% mixture displays the expected weight loss in the temperature range of 200°C to 300°C; however, the weight loss does not represent the 5% w/w sample of As_2O_3 that was added to the flyash. At higher temperatures it is also noted that the total weight loss is not 5% greater than the flyash, indicating quantitative determination of a volatile compound content is unlikely.

In addition to TGA's, the flyash and flyash plus 5% As_2O_3 were subjected to DSC analysis to evaluate its potential of sample evaluation and to determine if the As_2O_3 reacts with the flyash before being fully volatilized. The DSC on the flyash showed a large sharp endotherm at 65°C and other small endotherms at 120°C, 150°C and 180°C. A broad exotherm centered at 540°C also is apparent. The run was terminated at 650°C because this is the upper temperature limit of the aluminum sample pans. The scan of the sample containing As_2O_3 shows the same sharp endotherm at 65°C, an endotherm at 150°C and a small broad endotherm centered at 230°C. As in the flyash sample, an exotherm is noted at higher temperature; however, it is shifted up to 560°C. The additional endotherm at 230°C that is present in the 5% As_2O_3 sample is assigned to the volatilization of the As_2O_3. No apparent (exothermic) reaction takes place between the As_2O_3 and the flyash and it should be expected that all of the As_2O_3 will excape during heat up. Failure to observe this result could potentially be attributed in part to surface absorption of the oxide to the flyash or to a

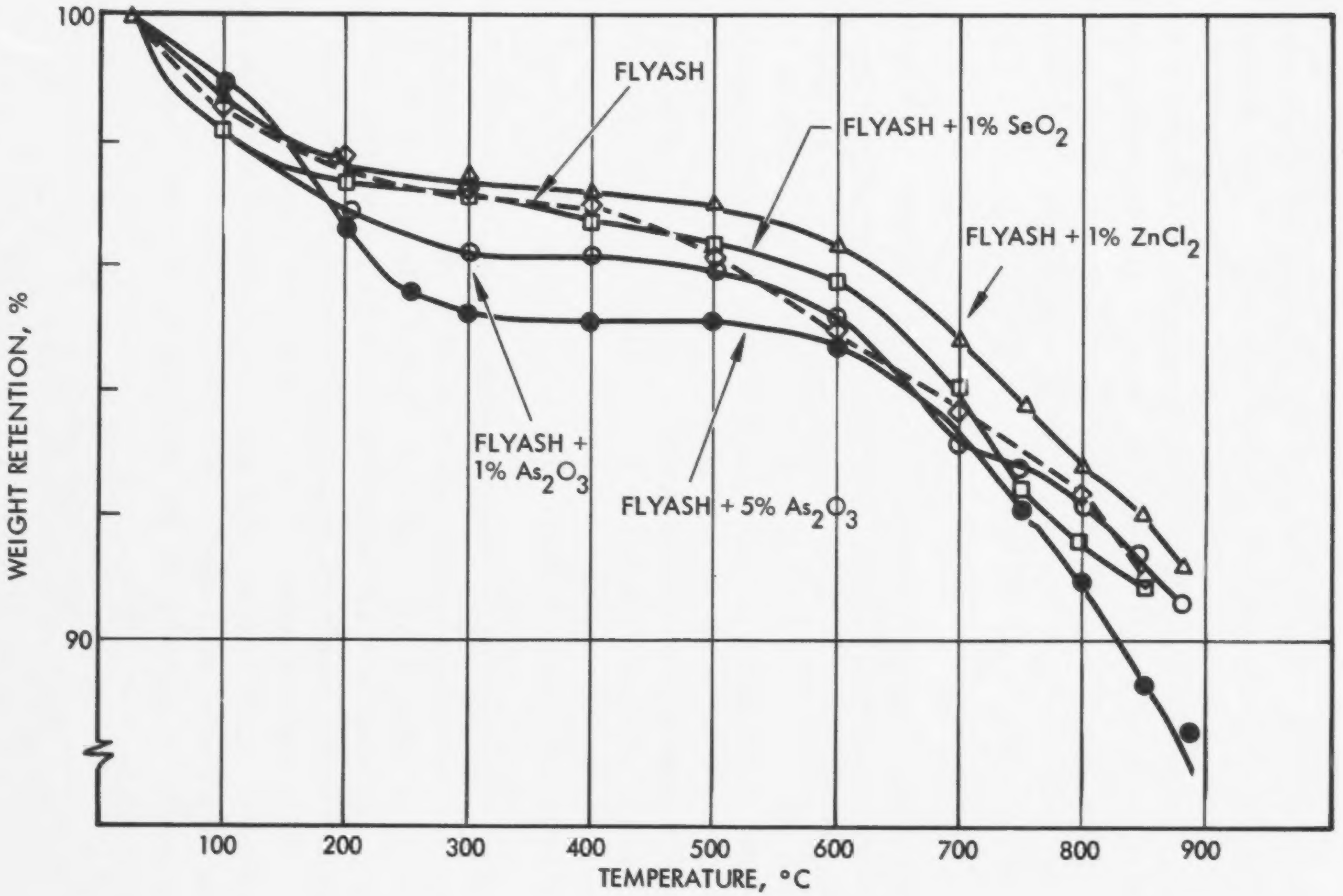


Figure 13. TGA's of Flyash and Model Compounds

non-homogeneous mixture that was used in the TGA runs. (That is, a small portion of the prepared mixture was used in a TGA run.)

It was concluded that this technique is useful in determining the gross thermal characteristics of a sample. For example, a TGA run could provide information as to the amount of moisture in a sample, likely decomposition temperatures of the mixture components, and overall thermal stability. This type of information could be of value, for example, in selecting a drying cycle for a mixture prior to analysis. However, determination of small quantities (<1%) of materials does not appear to be very promising unless one can obtain reproducible results from a known mixture. This obviously was not the case for the FBC material.

Special Projects Results--

Proton Induced X-Ray Emission (PIXE) -- Energetic protons from a nuclear accelerator can be utilized to provide a technique for quantitative, multi-elemental analysis. The sample is prepared as a thin film and bombarded with a beam of protons which produce characteristic X-ray emission from all elements in the sample. The X-rays are detected by an energy-sensitive semiconductor device and the data is processed by an on-line computer. Proton excitation provides much better sensitivity than electron excitation because the yield of characteristic X-rays compared to background radiation is much higher. Protons have an advantage over X-ray excitation because good sensitivity can be obtained for a much larger group of elements.

Quantitative analysis of the broad range of elements excited by energetic protons is made possible by the use of an energy sensitive X-ray detector and on-line computer data processing. A Si-Li detector provides good energy resolution and high sensitivity for X-rays emitted from all elements heavier than Mg. Electrical pulses from the detector are processed in an advanced electronics system and sent to an on-line computer. While the computer is recording X-rays from one sample it is also processing data from the preceding measurement. The analysis results are available from the computer at approximately the same time that new data accumulation is finished.

When a sample has only trace quantities of elements in a lightweight matrix, PIXE analysis is not complicated. A common example is the analysis of solids from an air sample collected on a hydrocarbon filter. However, with most solid samples, one must deal with the problem of intense X-rays from elements which are present in high concentrations. In order to apply PIXE as a general analysis tool, it is necessary to use X-ray filters, advanced electronic systems, and computer programs.

PIXE Results-- A comparison of the As values obtained by PIXE was made to the Level 1 procedure. The fly ash samples were prepared by aqua regia extraction and then analyzed by arsine generation and quantitated by AAS. The PIXE analysis was performed by Dr. Paul Simms at the Purdue University. The results are shown in Table 11. It should be noted that the only preparation required for PIXE was mounting the solid sample on a Mylar film. The excellent agreement shows that PIXE might be useful as a supplement to Level 1 analysis for As, and possible Hg and Sb. Since PIXE can also be used to monitor major components, it can be used to quantitate major concentration elements which exceed SSMS limits.

TABLE 11. PIXE VS. AAS As PROCEDURE

Sample	PIXE (ppm)	Wet Chemical (ppm)
Mechanical Precipitator	53	46
Electrostatic Precipitator	213	202
HVSS Cyclone Catch	163	149
HVSS Filter Catch	1681	1395

SEM-EDX/Electron Probe Microanalysis-- The samples must be conductive when analyzed by SEM-EDX or Electron Probe Microanalysis (EPMA). This can be accomplished by placing them on a conductive sample stage or by coating with a film of conductive material, e.g., C, Pt, or Au. The coating technique can interfere with surface topography and any subsequent EPMA analysis; therefore, the use of a conductive stage is preferred. In these experiments, the samples were "floated" over the face of the Cu stage with acetone and run directly.

A problem was encountered with small, thin particles. These were analyzed with EDX and the composition of the copper stage was obtained rather than that of the sample. New sample stages were prepared by plating a thick film (3 Mil) of high purity gold on the copper substrate. Gold will not interfere, as does copper, with these samples. Also the Au stages can be directly placed in the EPMA without further preparation.

It was found that samples prepared by the SEM operator and scanned using the instrument for general morophological characteristics takes a significant amount of time. It is much more efficient to mount the samples using an optical microscope and then direct the SEM work. This can be done using a scribed sample stage. This will increase the quantity of SEM images that can be conducted for the instrument time requested. Charging of the particles may still cause blurring of the pictures obtained. The EDX appears to be acceptable for bulk analysis but is not sensitive to trace elements and is not capable of detecting any elements lighter than sodium.

2.5.4 Recommendations

Based on this the work completed in this task, the following areas should be investigated:

- Literature search — The initial literature search performed in this task developed a large data base of information. This activity has been continued to a limited extent during the course of Task 7. It is recommended that a general task be initiated to perform a continuing and comprehensive search for inorganic compound analysis methods.

- XRD — Our work has shown that XRD analysis of environmental samples is possible, but that several problem areas still exist:

    1) Sample mounting — methods need to be developed to either analyze material impacted directly on glass fiber filters or to develop removal techniques to separate the sample from the glass fiber filter without sample modification. One possible technique is to use Freon as the solvent and and ultrasonic cleaner to break-up the filter. Filtration or density gradiant separation could be used to remove the glass fibers.

    2) Sensitivity — Improved sensitivity through computer averaging techniques should be studied to improve the sensitivity of XRD.

- Infrared Analysis — FTIR has been shown to have certain advantages over conventional IR in the areas of sensitivity and spectra manipulation. Work should be continued to:

    1) Study the effects of sample conditioning on the structure of the compounds. Work is needed to "normalize" samples so that spectral shifts due to hydration, crystalline form or sample matrix do not occur or are identified.

    2) Study the direct analysis of material impacted on glass filter to see if this information can be used to supplement direct XRD analysis.

    3) Study the subtraction capability of FTIR to establish guidelines on subtraction procedures for complex mixtures. The goal is to subtract different samples from each other to emphasize differences in the samples, such as particulate matter collected at the inlet or outlet of an FGD.

- Surface Analysis — SEM-EDX is adequate for high resolution morphology studies of environmental particles, however, EDX is not surface limited. Three separate techniques should be studied for their use for elemental depth profiling:

    1) Scanning Auger Microanalysis (SAM) — This technique is surface specific and provides images of the particle on surface analyzer surface structures. Argon ion etching is also possible.

    2) ESCA — This technique provides elemental surface data information and can determine the oxidation state of many elements. This technique is especially useful for sulfur.

    3) Secondary In Mass Spectrometer (SIMS) — This technique provides a wider elemental range and higher sensitivity for elemental depth profiling.

2.6 TASK 8 SAMPLING AND ANALYSIS OF REDUCED INORGANIC COMPOUNDS

2.6.1 Objective

The objective of this study was to develop sampling and analysis techniques for the determination of emission rates of specific reduced organic compounds from stationary sources. The sampling and analysis techniques established provide an accuracy of ±25%, a precision of ±30% and are applicable to various industrial sources. For this work, reduced inorganic compounds were defined as any metal or non-metal which is bound to hydrogen, is in its zero oxidation state, or is bound to carbon.

2.6.2 Approach

The task was divided into five subtasks to better define the approach taken:

- Subtask 1 — A literature survey was conducted to define the sampling stream parameters of those sources suspected of producing reduced inorganic effluents. The parameters defined were used to determine the procedures to be used for sampling and analysis and predict possible problems and interferences.

- Subtask 2 — A second literature review was made to define the state-of-the-art for reduced inorganic compound sampling and analysis. This review resulted in a preliminary sampling and analysis plan for a specific set of reduced inorganic compounds.

- Subtask 3 — The procedures outlined as a part of Subtask 2 were tested and verified in the laboratory. The laboratory effort was devoted to determination of possible interferences, detection limits, special sampling hardware, etc.

- Subtask 4 — When a sampling and analysis procedure was shown to be effective in the laboratory, it was further tested in the field. The field test was used to critically evaluate the laboratory procedure on "real" samples and to better determine interferences and effects of stream parameters on sampling techniques.

- Subtask 5 — Documentation of findings was the result of this task. A technical manual and guidelines document on sampling and analysis of reduced inorganic species was ultimately produced.

2.6.3 Technical Discussion

Identification of Processes Generating Streams Containing Reduced Compounds --

Literature searches, supplemented by analysis of the chemical and operating parameters of individual processes and contacts with knowledgeable persons, were used to identify 1) industries which could be sources of reduced inorganic species; 2) the nature of the reduced compounds in specific effluent streams; and 3) methods which can be used to sample the identified streams.

As a result, the following process parameters were selected as conducive to the formation of reduced species:

- Operations in which hydrogen is present in significant quantity.
- Operations which are oxygen deficient.
- Processes which contain metal oxides in a partially reduced state, because such oxides may interact with various agents to form reduced species.
- Processes which generate substantial quantities of carbon monoxide or nitrogen oxide in the presence of those elements capable of forming carbonyls or nitrosyls.

Sixteen processes employed in at least seven industries were identified as potential sources of effluents containing reduced inorganic species. The identified industries are listed in Table 12, which also highlights characteristics of the effluents from the process operations of interest.

Sampling Techniques for Reduced Inorganic Species--

Sampling procedures were chosen with the goal of obtaining samples which could be analyzed within an accuracy of ±25%. Three practices were found in common which were necessary to accomplish this: 1) samples must be time integrated to account for process operating variances; 2) sampling techniques must be sensitive enough to measure volumes, weights, and flows with greater accuracy than ±25% and 3) sample contamination or loss must be avoided.

TABLE 12.

INDUSTRIES AND PROCESSES PRODUCING REDUCED INORGANIC SPECIES

	Effluent Characteristics from Predominant Process Operations					Reduced Species Present in Primary Effluents	
	Particulate Data						
Process Idenfication	Size Distribution	gr/SCF	Flow Rate ①	Temperature °F	Moisture: Vol %	Cited From Literature	Probable Stream Based on Chemistry
1) Steel Plant						Ⓖ	Ⓖ
ⓐ Blast Furnace	15-90% < 74μ	4-30, 7-10 avg.	ⓐ 40-140 ⓑ 60-138	390 at throat 3000 at Furnace	9.6	H_2 H_2S	FeS, MgS, MnS COS, CaS, $Fe(CO)_5$, Mn $(CO)_{10}$
ⓑ Sinter Plant ① Windbox:	15-45% < 40μ 9-30% < 20μ 4-19% < 10μ 1-10% < 5μ	0.2-3.2	ⓐ 30-460 ⓑ 148-230	100-400	2-10		Ⓖ COS, $Fe(CO)_5$
② Discharge end:	80% < 100 10% < 10	1-5	ⓐ 0.03-0.2	100-300			Ⓖ COS, $Fe(CO)_5$
ⓑ Coke Ovens						Ⓖ	Ⓖ
① Oven off gas	Highly Variable	1-15	2.1 M ft^3 per charge	≤1832	Variable depending on point in coking cycle	$Ni(CO)_4$, HCN, NH_3 H_2S, H_2, COS, CS_2, NH_4CN	AsH_3, SbH_3 The formation of a variety of hydrides, carbonyl, and metal sulfides is possible.
② Quench Tower	95-97% > 47μ	0.05-0.1	900 M ft^3 per quench	140-150	Effluent consists primarily of steam	Ⓖ Ⓛ $Ni(CO)_4$, HCN, H_2, NH_3, NH_4CN, COS, CS_2	Ⓖ Ⓛ The formation of a variety of hydrides, carbonyls, and metal sulfides is possible.
③ Sour Quench Water	Not Applicable		Water usually sluiced; flow variable and cyclic			Ⓛ Cyanide and ammonia species are cited in the literature. Distinct compounds are not identified.	Ⓛ Metal sulfides, cyanides, sulfur cyanides, and reduced ammonia species.
2) Coal Fired Boilers	25% < 10 49% < 20 79% < 44	2.9 to 3.7 avg.	ⓐ 297-397 ⓑ 362-434	245-258	6.4	Ⓖ $Cr(CO)_6$ has been cited in the literature, although this is not a reducing atmosphere.	Ⓖ If, however, the formation of $Cr(CO)_6$ is possible, the existence of other carbonyls is also possible. CO concentrations may be as high as 70 ppm.

(Continued)

① Flow rate is expressed in: ⓐ M SCFM or ⓑ M SCF/ton of product processed.

Ⓖ = gaseous phase; Ⓛ = liquid phase; Ⓢ = solid phase

TABLE 12. (Continued)

	Effluent Characteristics From Predominant Process Operations					Reduced Species Present in Primary Effluents	
	Particulate Data						
Process Identification	Size Distribution	gr/SCF	Flow Rate	Temperature ^{o}F	Moisture: Vol %	Cited from Literature	Probable Stream Based on Chemistry
Refinery Operations							Ⓖ Ⓛ
ⓐ Claus Plant Tail Gas						Ⓖ H_2S, COS, CS_2, NH_3, HCN	Spent chemicals from acid gas amine solution regeneration = carbonyls, cyanides, sulfides.
ⓑ Fixed Bed Catalyst Regeneration				Fixed and moving bed regenerable catalysts function at about 850 to 1000°F at 300 to 700 psig		H_2S, COS, CS_2, $Ni(CO)_4$ $[Co(CO)_4]_2$	$Mo(CO)_6$; the formation of various metal sulfides, hydrides and carbonyls probable.
ⓒ Moving Bed Catalyst Regeneration						H_2S, COS, CS_2, NH_3, $Ni(CO)_4$, HCN	
ⓓ Fluid Coker off-gas						H_2S, COS, CS_2, NH_3, RCN, $Ni(CO)_4$	Metal sulfides and carbonyls probable.
Coal Conversion ①							
ⓐ Gasification and Liquefaction Operations						Sulfides in rinse solution and particulate. The full spectrum of reduced species are formed in gasification. Many of these are incorporated into the quench water.	Dryer off gases may contain carbonyls.
① Coal Preparation							
② Quenching and Cooling							
③ Fixed bed Catalyst: Regeneration	Same parameters and species as defined under "Refinery Operation," above.						
④ Sulfur Plant:	Same as Claus Plant above.						
⑤ Tar Separation						Ⓛ $Ni(CO)_4$, NH_4CN, HCN	Ⓛ The existence of Arsine, Stibine, carbonyls and sulfides is probable.
Fertilizer Manufacturer	6.3% < 5μ, 12% < 10μ, 29% < 30μ, 34% < 40μ	0.7 to 4.0	ⓐ 16.5 (one unit)	201		Ⓖ NH_3, HF	Ⓖ Cyanides, Nitrosyls.

① Stream parameters are highly variable depending on process design, see text.

(Continued)

TABLE 12. (Continued)

Process Identification	Effluent Characteristics From Predominant Process Operations					Reduced Species Present in Primary Effluents	
	Particulate Data						
	Size Distribution	gr/SCF	Flow Rate	Temperature °F	Moisture: Vol %	Cited from Literature	Probable Stream Based on Chemistry
Forest Products Industry							
ⓐ Kraft Pulp Mills							
① recovery furnace	50-85% < 2μ	3-8 avg. 3-8	ⓐ 20-568 ⓑ 278-568	270-650 avg. 350	20-40	Ⓖ H_2S, Na_2S	Ⓖ COS FeS
② lime kiln	95% < 25μ	3-20	ⓐ 7-50	400-900	400-600 lbs/air dried ton	Ⓖ H_2S	Ⓖ COS, FeS, MgS, CaS
③ smelt dissolving	90% < 5μ	0.17-1.3	45 SCF/air dried ton	170-200	670 lbs/air dried ton	Ⓖ H_2S, Na_2S	
Primary Nonferrous Metals Industries							
ⓐ Copper							
① roasting furnace	15% < 10μ	6-24	ⓐ 60-131	600-890		Ⓖ Cu_2S FeS	Ⓛ Liquid tailings from refining operations are likely to contain selenides, tellurides, and sulfides.
② electrolytic refining*						AsH_3	
ⓑ Lead							
① sinter machine	100% < 10μ	0.4-4.5	ⓐ 140 ⓑ 130	250-600		Ⓖ	Ⓖ PbS, ZnS
② Blast furnace	0.03 to 0.3	1-11	6-14	150-250		PbS	ZnS, CdS, COS
ⓒ Zinc							
① roaster	14% < 5, 31% < 10 70% < 20	5-65	25-30	730-900		Ⓖ ZnS	
② sinter machine	100% < 10	0.4-4.5	140	320-700	Dew Point: 122-140		Ⓖ ZnS, PbS, CdS
ⓓ Aluminum							
① reduction cell	Submicron particulate	0.03-2.0	2000 to 4000 CFM/cell			Ⓖ H_2S	Ⓖ COS, Na_2S, CaS, Al_2S_3 Electrode is concerned in the reduction process; considerable CO is formed. Metal carbonyls may therefore result.

*Process data for electrolytic refining is highly variable; literature does not site specific flow data.

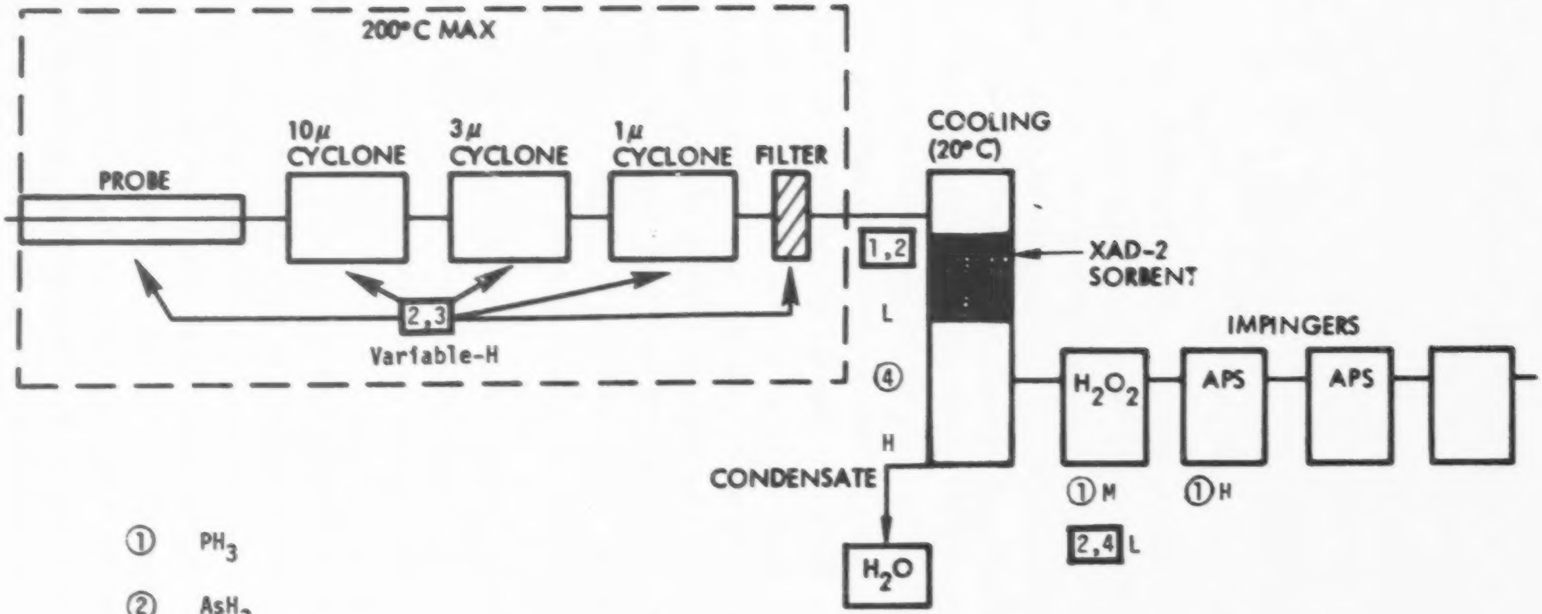
The sampling techniques chosen for use with specific process streams containing reduced inorganics included:

1) Solid — integrated composite
2) Liquid — integrated composite
3) Gas — fugitive emissions
4) Gas — time integrated (non-particulate)
5) Gas — SASS train (particulate)

Although each method has restrictions and limitations, the applicability of the SASS train was deemed worth particular study because it generally is not suited for sampling reactive inorganic species for subsequent compound identification. The levels anticipated for reduced species are generally low and chemical modification by the act of sampling will in some cases not allow for subsequent analysis. Sampling for solid reduced inorganic species from particulate material may be possible using the SASS; however, reduced inorganic gases will either be lost or chemically modified due to their inherent susceptibility to oxidation or thermal instability. By studying the chemistry of several of the reduced species, an estimation of the probable locations of specific compounds in the SASS train was made. This information is shown graphically in the following figures: Figure 14, PH_3, and SbH_3; Figure 15, reduced sulfur compounds, H_2S, COS, and RSH; Figure 16, reduced nitrogen compounds, NH_3, HCN, and $(CN)_2$; and Figure 17, Hg, Se, and metal carbonyls.

Sampling and Analysis of Gaseous Reduced Inorganic Compounds--

The sampling and analysis procedures presented in the final report on this task were compiled from literature searches, developed or modified in the laboratory, and, in three cases, tested during a field study on an actual source of reduced inorganic emissions -- the Paraho Shale Oil Demonstration Plant. The procedures are detailed and limited in application to specific reduced chemical compounds. Some, in fact, are unique for a single substance. Due to the generally unstable nature of reduced inorganic compounds, the procedures require specialized sampling equipment and techniques. For the purpose of sampling and analysis, reduced inorganic compounds can best be divided into groups based on their acidic, basic or neutral characteristics. Stability of the species to oxidation is also an important parameter as illustrated by such metal hydrides as phosphine, arsine and stibine. Acidic species of interest include hydrogen sulfide, mercaptans and hydrogen cyanide. The basic



① PH_3

② AsH_3

③ SbH_3

④ Organometallic forms of P, As, and Sb

L = Small concentration

M = Moderate concentration

H = Large concentration

Figure 14. SASS Distribution for PH_3, AsH_3 and SbH_3

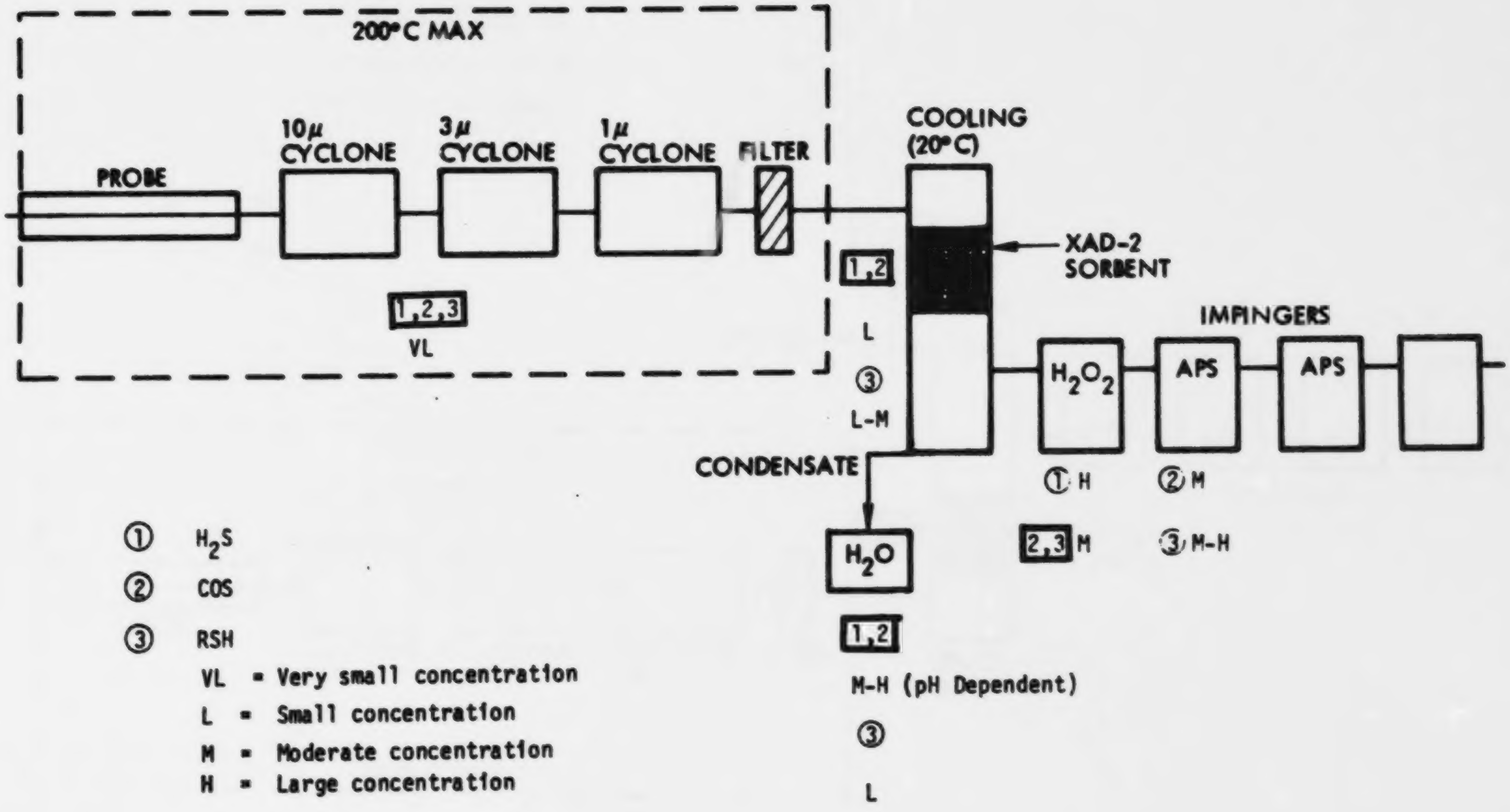


Figure 15. SASS Distribution of Reduced Sulfur Species

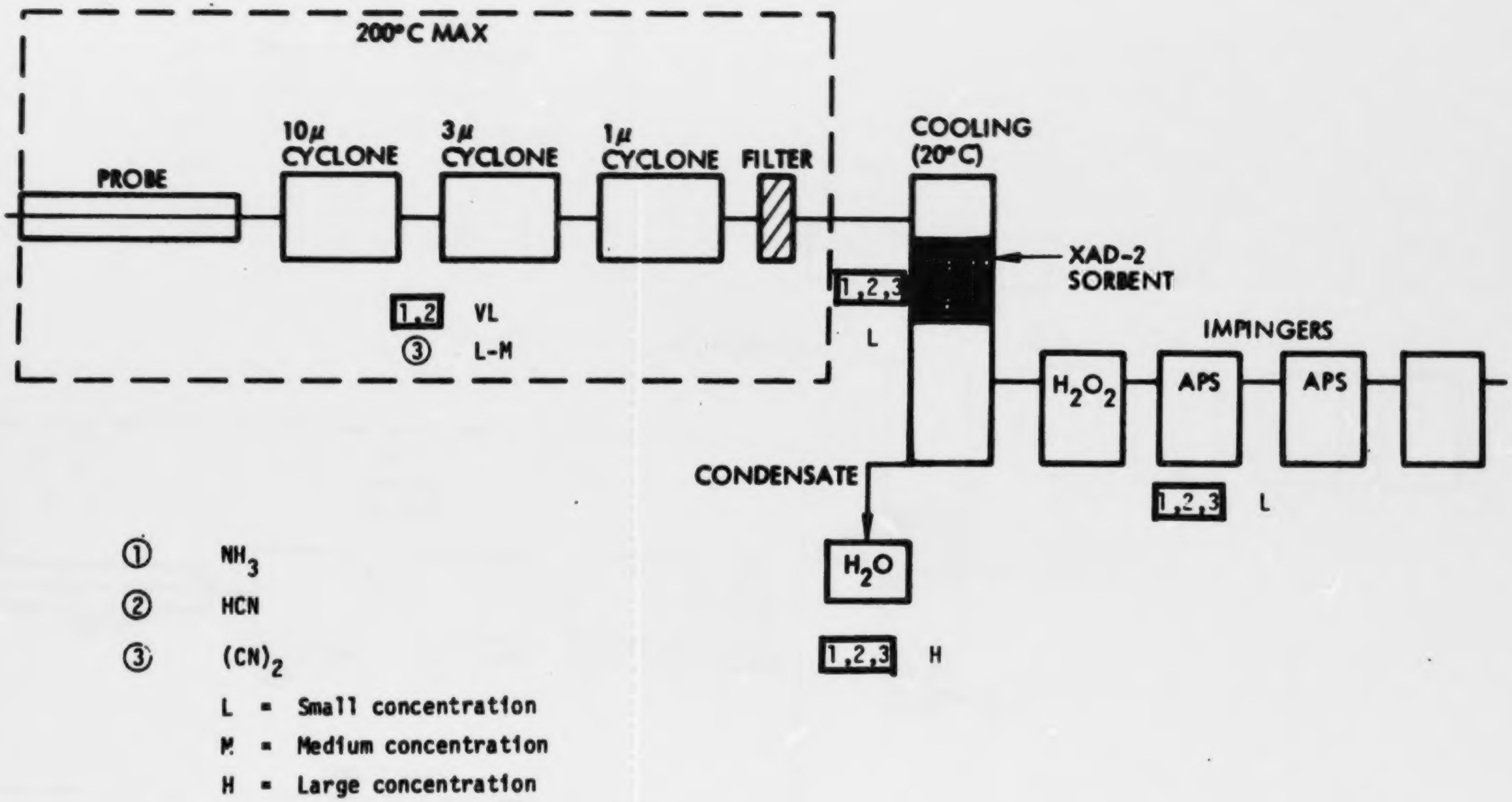


Figure 16. SASS Distribution of Reduced Nitrogen Species

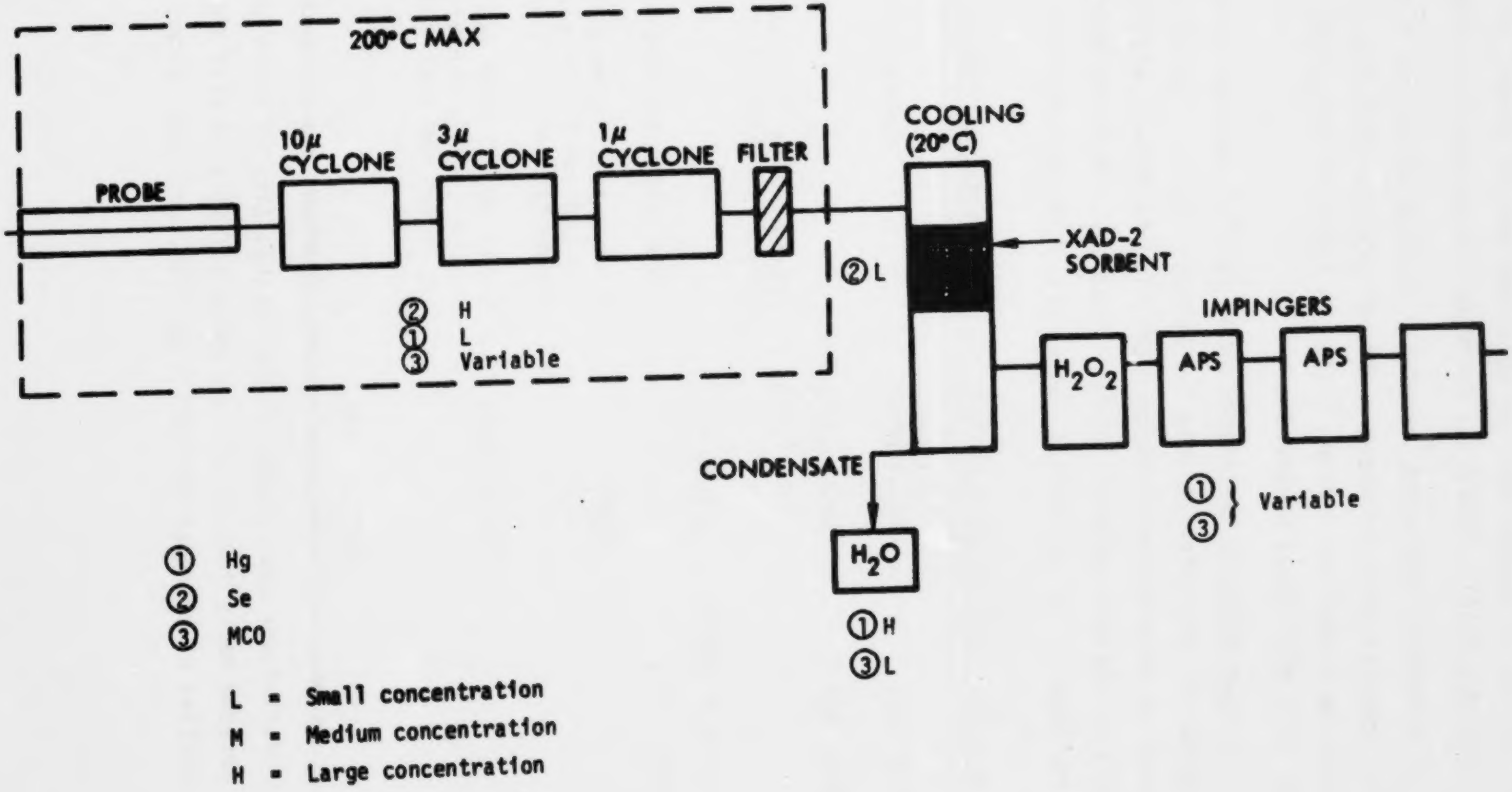


Figure 17. SASS Distribution of Hg, Se, and MCO

group consists of ammonia and low molecular weight amines, while the neutral class includes metals, hydrides, cyanogen and carbonyl sulfide.

A thoroughly developed, carefully studied method for the collection and species identification of mercury and mercury compounds has recently been published by Braman and Johnson (11). In light of this, this study did no further work with these compounds.

Impinger trapping techniques using several impinger solutions were investigated for all other reduced inorganics. Overall, entrainment of the compounds of interest in a reactive solution is direct, efficient and often amenable to analysis without further treatment. Table 13 below summarizes the requirements for collecting the several reduced species:

Table 13. Collection Solutions for Representative Reduced Species

Compounds	Impinger Solution(s)	Comments
H_2S, RSH, HCN	Basic $CdSO_4$	
HCN	Conc. H_2SO_4	Pre-scrub NH_3 from gas stream with dilute HCl containing impinger.
NH_3, low M.W. amines	Dilute HCl	
PH_3, AsH_3, SbH_3	H_2O_2	Other oxidizing reagents possible.
Se	H_2O_2	Other oxidizing reagents possible; also can use filter paper wetted with strong cyanide solution.
COS	$CaCl_2$+NH_4O_4	Pre-scrub H_2S from gas stream with aqueous $Cd(OH)_2$ containing impinger. Post-scrub CS_2 with KOH/alcohol solution.
$(CN)_2$	Dilute NaOH	

A preliminary examination of the capabilities of solid sorbents was made. Because early results did not compare favorably with the efficiencies and capacities of impinger collection systems, work was halted.

Species of Interest	Solid Sorbent	Test Results
H_2S	Tenax GC	Inadequate
	XAD-2	Inadequate
	Porapak QS	Marginally acceptable at 0°C - problem with low breakthrough volume.
NH_3	Chromosorb 103	Low breakthrough volume even at 0°C; convenient if effluent gas stream has high NH_3 concentration.
COS, $(CN)_2$	Porapak QS	Low breakthrough volume prevents use with trace levels in effluents.

When field analytical equipment is available and the reduced inorganic sample concentration in the gas stream is relatively high, grab sampling is the preferred method. Rapid analysis in the field eliminates the requirement for efforts to stabilize the samples and could be less expensive as well.

The chemical state of the sampled species often dictates the analysis technique to be used. Impinger solutions, if relatively free of interfering materials can often be analyzed directly using ion specific electrodes, or such classical wet chemical techniques as titration or gravimetry. For more complex mixtures, regeneration of the original sample is often required to minimize interference problems. For samples adsorbed on solid substrates, thermal desorbtion or solvent extraction may be necessary prior to analysis. Grab samples may be analyzed directly or after concentration.

The procedure to be used for analysis is dependent on the sample matrix, possible interferences and the sampling technique. The techniques used in this study on impinger entrained samples are summarized below. Details of all procedures investigated were presented in the task final report.

Compounds of Interest	Sample Preparation	Analytical Technique
H_2S, RSH, HCN	Acidify and purge	GC with Porapak QS column using TC detector (Figures 18, 19)
NH_3 and amines	Neutralize, steam distill, and purge	GC with Chromosorb 103 column using micro-TC detector

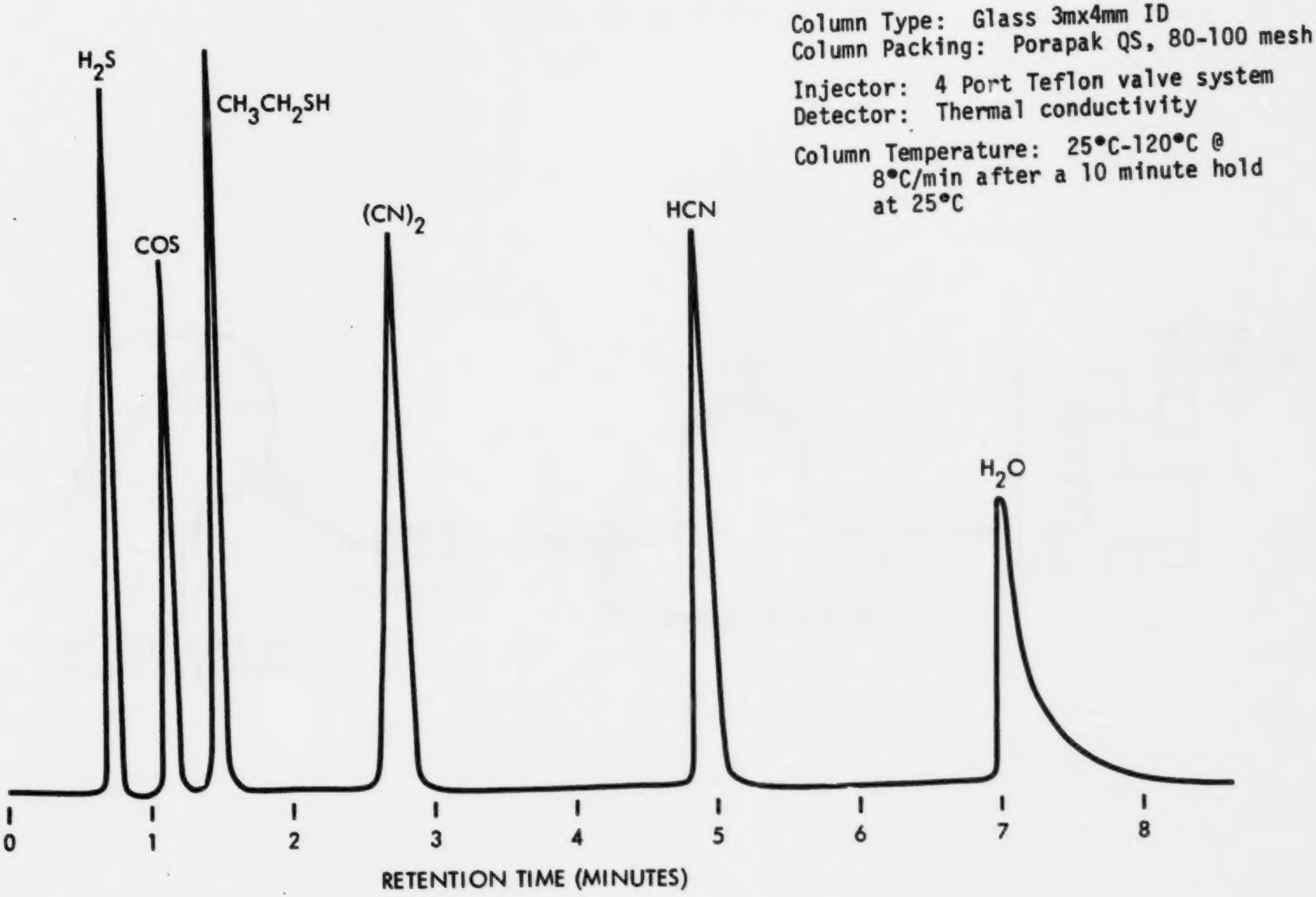
Compounds of Interest	Sample Preparation	Analytical Technique
PH_3, AsH_3, SbH_3	Destroy excess H_2O_2, acidify, reduce using $NaBH_4$, (Figure 19)	GC/MS (Figure 20) Much less sophisticated technique desirable for routine work - perhaps GC-FPD
Hg,	Thermal desorption	AA
Se	Add 1% nickel to convert sample to selenide	AA
COS, CS_2	Add barium	Gravimetric determination as $BaSO_4$.
$(CN)_2$	—	Modified Werner procedure (colorimetric)

Field verification studies of the ammonia/amine procedure, the hydrides procedure and the carbonyl sulfide procedure were successfully performed on samples obtained at the Paraho Shale Oil Demonstration Plant. A total of four individual samples were obtained from the recycle gas stream. These samples were analyzed in triplicate using the procedures previously described. The results of the analyses are presented in Table 14.

Table 14. Field Test Results for Arsine

Sample No.	Volume Sampled	Amount Arsine Detected	μg/M^3 Arsine
1	0.15 M^3	.025 μg	0.17
2	0.14 M^3	.035 μg	0.25
3	0.13 M^3	.045 μg	0.35
4	0.13 M^3	.060 μg	0.46

Arsine was the only hydride detected in the samples analyzed and no organometallic species were detected. The results of triplicate analysis of the same sample were within ± 20% relative. The deviation of the amount of arsine found between samples is probably due to the small sample volumes obtained and the non-homogeneity of the recycle gas stream due to process variations.



Column Type: Glass 3mx4mm ID
Column Packing: Porapak QS, 80-100 mesh

Injector: 4 Port Teflon valve system
Detector: Thermal conductivity

Column Temperature: 25°C-120°C @
8°C/min after a 10 minute hold
at 25°C

Figure 18 Typical Chromatogram for Reduced Inorganic Gases Using Porapak QS

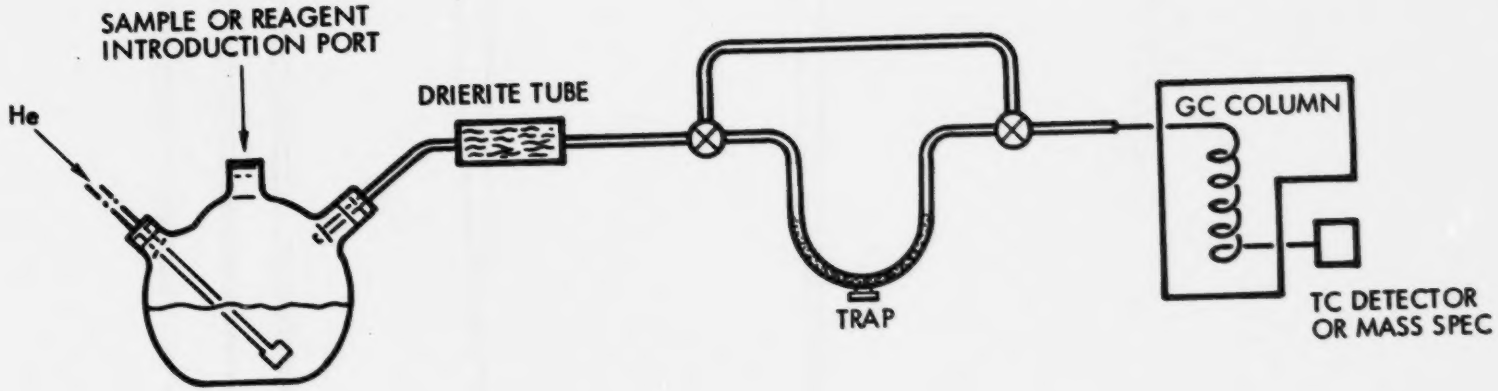


Figure 19 Reduced Gas Evolution Apparatus

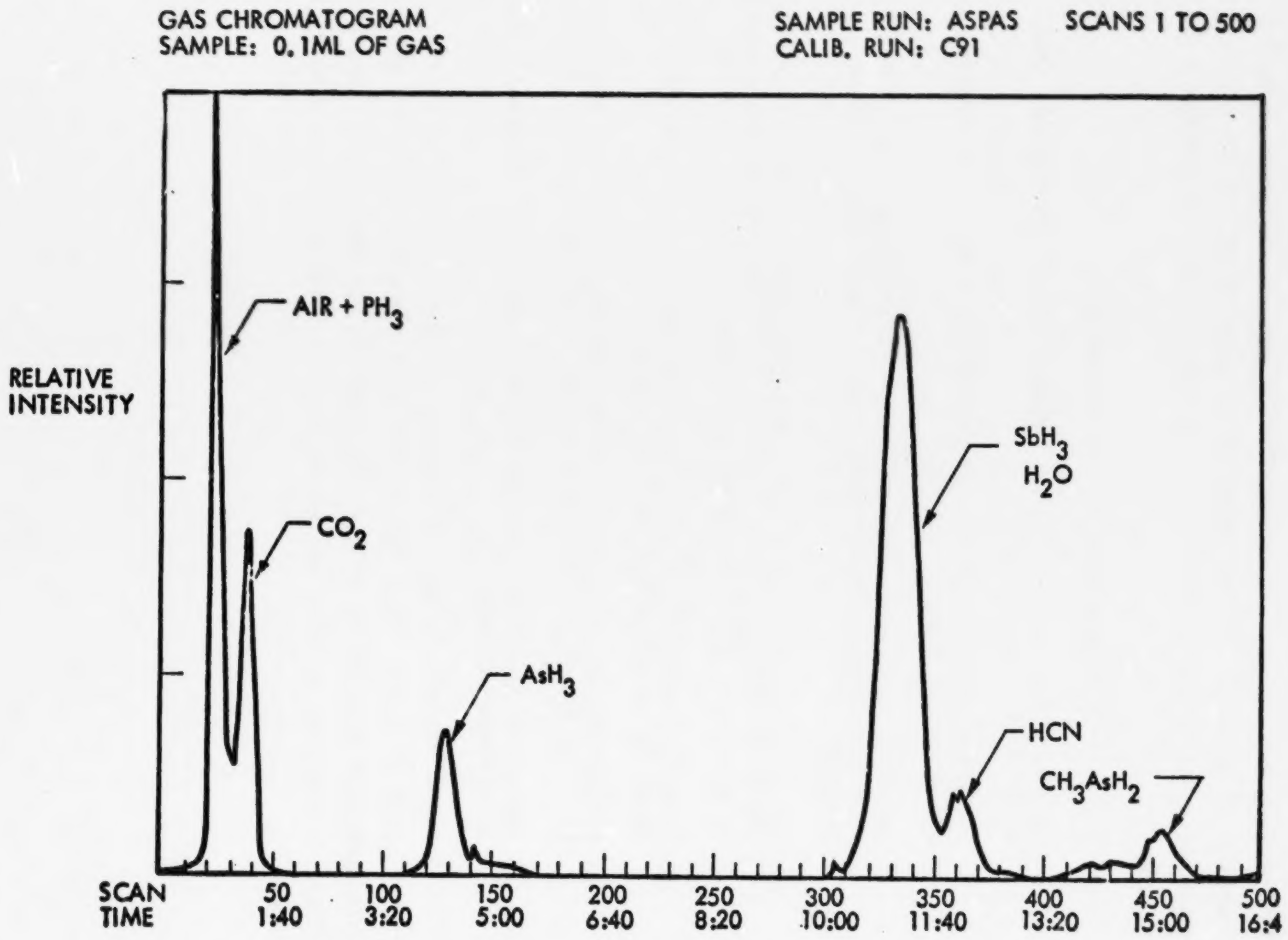


Figure 20 Resconstructed Gas Chromatogram of The Hydrides Produced by Reduction Procedure

2.6.4 Recommendations

A description was provided in the final report of the methodology for the sampling and analysis of representative reduced inorganic compounds from a variety of sources. Further research is required before the proposed methodology can be routinely used in the field. Specific problem areas include:

- Evaluate complex samples for interferences.
- Determine the recovery of all reduced species in mixtures described by a statistical matrix.
- Determine the storage life of samples collected, i.e., impinger and adsorbent trapped samples.
- Complete characterization of Porapak QS and other specialized materials for use in adsorbent traps for selective compound sampling.
- Design and evaluation of cartridge-type adsorbent traps that can be stored for extended periods before and after use without changes in efficiency for sampling or degradation of trapped samples.
- Establish conditions to permit rapid sampling and analysis of higher molecular weight amines and mercaptans.
- Choose from existing sources or design selective detectors for the identification and determination of reduced inorganic species.
- Improve or design new on-site monitors for reduced inorganic species in effluent streams.

The sampling and analysis of reduced inorganic species is a very important area of study. Very few current environmental assessment programs are using compound specific techniques for sampling and analysis. Therefore, little information is being gained on the true risk associated with a given source.

2.7 TASK 9 COAL MONITORING INSTRUMENTATION

2.7.1 Objective

The purpose of the task was to investigate the state of the art for continuous coal mass flow and composition measurements, both to determine current capabilities, and to investigate the need for EPA involvement in research and development efforts. The types of flow investigated were dry coal flow (typically on a belt) and coal-water slurry flow. Composition-type measurements are performed on small samples (few grams) with laboratory instruments and on dry slipstreams with various instruments currently under development. Measurement in slurries is presently limited to only slurry density.

2.7.2 Approach

The task was divided into the following items:

- Literature search
- Vendor and user search and contact
- Evaluation of information
- Calculations and analyses
- Field trip
- Preparation of final report

The literature and vendor searches were used to determine available instrumentation and status of instrumentation currently under development. Compiled information, along with user data, was then used to compare the various instruments. We then performed calculations and analyses of our own to determine system limitations and errors. A brief trip to the Pittsburgh/Morgantown area was undertaken to visit key facilities. A final report, in the form of a technical manual, was then prepared.

The only significant deviation from the original plan was a contractual one — shortly after its inception, this task was transferred to Contract 68-02-2613, where it became Task 2, "Evaluation of Equipment to Determine the Mass Flow of Coal in Process Streams." The latter task title is somewhat misleading, since composition as well as mass flow was considered. The title of the final report, "Assessment of Instrumentation for Monitoring Coal Flowrate and Composition," is indicative of the work performed.

2.7.3 Technical Discussion

The task was a paper study evaluation of instrumentation. The draft final report was issued at the end of February 1978, and was published in March of 1980. The draft report is a 150-page document. The Table of Contents is presented as Figure 21 on the following page.

The task logically divided itself into two areas: flow instrumentation and analysis instrumentation. The two areas differ widely not only in terms of being different types of measurements, but also in terms of state of development.

Coal flow rate instrumentation, especially for belt conveyors, is very accurate and reliable. Belt weighing devices are available from a large number of vendors, are relatively inexpensive ($5,000-$10,000 for a 1000 ton/hour capacity), and have accuracies in the range of ±0.1 percent to ±1 percent of reading. Vendor and literature data were obtained for this type of instrument, establishing wide availability and ease of use. Extensive talks were held with the Southern Weighing and Inspection Bureau, the acknowledged authority in this area (by the National Bureau of Standards). The Bureau's procedures for calibration and use of weigh belt devices is presented in annotated form as an Appendix to the final report. Belts are the most common means for short distance conveyance of coal at power plants.

Slurry flow measurement is not quite as accurate as conveyor belt measurements, but various techniques, most notably the electromagnetic flowmeter and the ultrasonic flowmeter, are readily commercially available. At present, there is very little demand for coal slurry flowmeters. This will likely change if long distance coal conveying in slurry pipelines becomes more widespread. It is clear that existing instruments will be usable for slurry applications which may arise in the future.

Figure 21. Table of Contents for Coal Monitoring Instrumentation Report

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Coal analysis instruments are of two types at present: laboratory instruments, which analyze a very microscopic sample of coal, and a variety of instruments, currently in various stages of development, which analyze part or all of an entire coal stream for a specific property such as moisture or sulfur. Laboratory instruments are dependent on complex sampling systems which extract a gram-sized sample from thousands of tons of coal. Also, there is necessarily a large time lag between the start of the sampling process and the completion of the analysis, meaning that this approach cannot be considered as continuous, real-time monitoring.

The goal of continuous monitoring appears to be best attainable by means of neutron activation instruments which can potentially analyze an entire coal stream. The approach operates on a "number of counts" basis, resulting in typical sampling times of about five minutes, with the output being an average reading for the sampling period. This time response is short enough that this type of device can be potentially used for control purposes. The development of neutron activation instruments for coal analysis has been led in the U.S. by the Morgantown Energy Research Center (DoE), which we visited in September 1977. At that time, we were told that a commercial neutron sulfur meter would probably be available within two to three years. We just received word, after sending the draft final report to MERC, that due to a "reordering of priorities," they are stopping work on neutron activation devices. This essentially means that no one in this country is presently doing work in this area.

2.7.4 Summary and Recommendations

The two-page summary section of the draft final report is presented below. The section will be modified in light of MERC's stoppage of their neutron activation work, and we will suggest that EPA consider the possibility of continuing this development of neutron activation analyzers.

Summary and Conclusions from "Assessment of Instrumentation for Monitoring Coal Flow Rate and Composition"--

Relevant techniques were presented in detail to give a general understanding and to give an idea of fundamental limitations. For example, a difference in ultimate utility between neutron activation devices and fluorescence radiation devices is shown by the fact that the former can operate with a penetration depth of order one meter, while the latter is limited to penetration depth of order one millimeter. This has strong implications on instrument configuration and utility.

In contrast to the rather sophisticated physics of coal analysis equipment, operation principles of most flow measurement devices are fairly simple. This simplicity has meant that flow measurement devices have been more easily developed, and have been in wide use for many years.

The material presented makes it clear that there are many techniques available for the measurements of interest. Availability of instrumentation, however, is another matter, especially in the case of coal analysis devices.

Instruments available now for coal analysis, with the exception of the neutron moisture meter, are capable of analyzing only small samples, which means that a sophisticated sampling system is required. The moisture meter itself is actually a hydrogen indicator, which means that the coal hydrogen content must be known independently to determine the moisture content. It has been the observation of MERC personnel that the hydrogen content in coal is in fact constant for a given coal type. Development of neutron activation instruments is not proceeding well, but a sulfur meter is expected as a production item within the next few yeats. It is hoped, this will be followed by modified versions capable of determining moisture and heating value. Neutron activation devices are of particular interest because they hold the promise of sampling entire coal streams, thus eliminating the major problem of obtaining a representative sample.

Weigh belt devices, either electromechanical or nuclear, and electromagnetic flowmeters (typically coupled with nuclear density gages) are the most used devices for dry coal flow measurement and coal/water slurry flow measurement, respectively, and will be acceptable for most situations. Weigh belt technology is especially highly developed, in part due to regulatory considerations. Intrusive devices may be applicable to slurry flow measurements, but this has not been clearly demonstrated as yet.

Weigh belt devices are sufficiently advanced, and their use in many situations sufficiently monitored by various regulatory agencies, that they should not need EPA attention. Similarly, electromagnetic flowmeters are a very standard item and do not appear to need attention, in terms of field evaluations for example, except in unusual circumstances. As far as other slurry flow measurement devices are concerned, we feel that a reasonable approach is to let vendors demonstrate that their devices are acceptable for (dense) coal/water slurries.

At such time as devices like the neutron sulfur meter become commerically available, IERL will likely wish to be involved in collaborative testing or other evaluation of the devices. This, however, will not be taking place for at least a couple of years.

Perhaps the most reasonable area for IERL investigation in the near future is instrumentation/control systems which make use of the kinds of instruments discussed in this report. The thrust of the investigation would be to determine how to make the best uses of available and soon-to-be-available instrumentation to control the operation of sources such as coal-fired utilities to minimize pollutant emissions through direct combustion control and/or optimizing operation of devices such as wet scrubbers. The greatest ultimate value of the instruments discussed herein is not just as monitoring sensors, but as components in an active control system, either on sources of direct coal combustion, or in coal cleaning plants.

2.8 TASK 10 COAL SULFUR MEASUREMENTS

2.8.1 Objective

The existing literature and pertinent authorities in the field of sulfur analysis were surveyed in order to determine existing sulfur forms methodology and the nature of the need for improved methodology. As a result of this survey a need for a more accurate organic sulfur analysis procedure was found. To fulfill this, TRW proposed two entirely new coal organic sulfur analysis procedures, both based on the selective removal of organic sulfur species present in coal via selective oxidation in an oxygen plasma instrument. The first procedure entailed the determination of organic sulfur by difference between two highly accurate and precise $BaSO_4$ gravimetric procedures. One on the starting coal and one performed on the resultant ash from an oxygen plasma decompositive of the coal matrix. The second procedure is the direct determination of organic sulfur by analysis of solid sorbents placed in the outlet line from the plasma asher used to sorb effluent SO_x species.

2.8.2 Approach

The first step in the verification of the proposed techniques was to search the literature for pertinent information dealing with the reaction of coal and coal minerals under oxygen plasma conditions. Few applicable documents were found. Because of the sparcity of applicable information a detailed evaluation of parameters that could affect the resultant accuracy and precision of techniques had to be performed. The laboratory evaluation of the two proposed techniques included the following:

1) Organic sulfur by difference between two $BaSO_4$ gravimetric procedures.
    - Feasibility of technique by comparison with organic sulfur values determined using ASTM D2492.
    - Reactivity of commonly occurring sulfide minerals under plasma ashing conditions.
    - Retention of sulfur by reaction with alkaline components of coal ash.
    - Accuracy and precision of the proposed HNO_3 extraction - $BaSO_4$ gravimetric analysis of the resultant coal plasma ash.

2) Direct determination of organic sulfur.

- Test various sorbent systems placed in outlet line of plasma asher for efficiency in removing SO_x species.

2.8.3 Technical Discussion

Coal Sulfur Forms Analysis with Indirect Determination of Organic Sulfur --

This analysis procedure is based on the selective removal of the organic matrix including organosulfur species from coal with a low temperature oxygen plasma. The inorganic sulfur species are quantitatively retained in the remaining ash. The inorganic sulfur in the ash is then extracted with dilute nitric acid and determined gravimetrically as $BaSO_4$ or speciated by ASTM D2492.

An evaluation of the data in the following sections shows that (1) the plasma procedure yields more accurate and precise results for inorganic and organic sulfur than the ASTM procedures; (2) naturally occurring sulfides are not affected under plasma conditions; and (3) organic sulfur species are not retained in the coal ash by reaction with alkaline compounds. The actual procedure has been optimized and is ready for testing in other laboratories.

Preliminary evaluation of the plasma ashing procedure was performed on 13 coals. The organic analysis results, Table 15 show that when the results are evaluated by coal basins, the ASTM-TRW-AA (an AA method developed by TRW) and plasma ashing procedures give essentially identical results while the standard ASTM procedure is low by 5-6%. In the case of the interior basin coals, the ASTM procedures are in good agreement while the plasma procedure is low by 10%. Three of these coals are from the same area and separate X-ray microprobe experiments have shown that they contain pyritic sulfur that is unextractable by the ASTM procedures. If this unextractable inorganic sulfur were extracted from the plasma ashed sample, this would be the cause of the lower organic number. Table 15 also shows analysis of sample treated by the Meyers Process. When before and after treatment values are compared, both the plasma ashing and the ASTM-TRW-AA procedures give consistent results, while the ASTM procedure gives widely discrepant results that tend to be significantly low for untreated Appalachian coals. Thus, in

TABLE 15. COMPARISON OF ORGANIC SULFUR DETERMINATIONS (% W/W BY DIFFERENCE)

Mine/Seam	Treated(T)[a] Untreated(U)	ASTM Procedure		Plasma Ashed
		Std.	TRW-AA	
E Seam (ROM)	U	0.48	0.46	0.52
	T	0.57	0.66	0.59
E Seam (Cleaned)	U	0.51	0.57	0.60
	T	0.60	0.68	0.65
Delmont (Upper Freeport)	U	0.25	0.79	0.81
	T	0.74	0.74	0.64
Bird (Lower Kittanning)	U	0.22	0.54	0.62
	T	0.50	0.55	0.55
Egypt Valley (Pittsburgh)	U	1.34	1.78	1.97
	T	2.03	1.81	1.81
Fox (Lower Kittanning)	T	1.18	0.90	0.90
	T	1.18	0.91	0.92
Williams (Pittsburgh)	U	1.19	1.48	1.42
	T	1.38	1.40	1.41
Lucas (Middle Kittanning)	U	0.32	0.50	0.49
Brookdale #77 (Lower Kittanning)	U	0.48	0.48	0.46
Old Ben #21[b] (Illinois #6)	U	0.63	0.60	0.45
Old Ben #24[b] (Illinois #6)	U	1.66	1.57	1.57
Old Ben #26[b] (Illinois #6)	U	1.38	1.34	1.19
Inland Steel[b] (Illinois #6)	U	1.81	1.80	1.66

a) Treated by Meyers Process to remove pyritic sulfur and adjusted for mineral matter (ash) changes.

b) Eastern interior basin coals.

reference to evaluation of coal cleaning processes, it appears that the ASTM procedure gives results dependent on coal processing while the other two procedures give results that are virtually independent of the history of the coal. A thorough comparative evaluation of the proposed procedure with ASTM methods was performed in triplicate on coals chosen to represent a variety of ten seams in the Appalachian and Eastern Interior coal basins.

From the tabulation of results in Table 16, it is seen that the ASTM titrimetric pyritic sulfur values exhibit a distinct negative bias when compared to values determined by AA. The exact reason for this bias is difficult to explain because the pyritic iron was determined on aliquots of the same extract for both procedures. In addition, the same iron standard was used for calibration of both analytical procedures. One possible explanation for this bias is loss of iron during the iron hydroxide precipitation, filtration and redissolution step which is necessary for the titrimetric procedure but not for the AA determination. This explanation is consistent when the total inorganic values (sulfate sulfur and pyritic sulfur) determined using the two ASTM procedures are compared to the TRW plasma-total inorganic values (Table 17); the results using the AA technique are in excellent agreement with the values obtained in the plasma ash procedure for the Appalachian coals. This agreement for total inorganic sulfur is directly reflected in the organic sulfur values contained in Table 18. The ASTM analyses of Eastern Interior Coals exhibit a positive bias for organic sulfur when compared with the plasma procedure. This bias probably is the result of the presence of very fine pyrite present in these coals which is not extracted with nitric acid in the ASTM procedure. This is substantiated by the electron probe microanalysis studies which show measurable amount. The presence of very fine pyrite can also explain the large differences in total inorganic sulfur experienced with the tailings sample.

Additional experimentation was performed on 10 coals to test the application of the ASTM sulfur forms extraction procedure on the plasma ash and to compare the corresponding analysis of the whole coal. ASTM D2492 was used for both sulfate extraction and analysis. The analysis of pyritic iron in the HNO_3 extract was performed by the TRW-AA atomic absorption method in both cases rather than a proposed ASTM-AA method. However, this was done because TRW has found the ASTM method to be considerably less

TABLE 16. COMPARISON OF SULFUR FORMS ANALYSIS METHODS

Mine	Coal Seam	Coal Basin	Total Sulfur		Pyritic Sulfur[1]-ASTM		Sulfate Sulfur[3] ASTM	Total Inorganic TRW Plasma Ash
			Eschka	Leco	Titration[3]	AA[2]		
Old Ben #21	Illinois #6	Eastern Interior	1.11 ±0.032	1.28 ±0.030	0.32 ±0.045	0.48 ±0.066	0.08 ±0.000	0.71 ±0.011
Old Ben #26	Illinois #6	Eastern Interior	2.26 ±0.031	2.21 ±0.031	0.65 ±0.036	0.77 ±0.006	0.16 ±0.006	1.25 ±0.015
Inland Peabody	Illinois #5	Eastern Interior	3.24 ±0.012	3.11 ±0.071	0.94 ±0.028	1.03 ±0.006	0.38 ±0.012	1.59 ±0.015
Martinka	L. Kittanning	Appalachian	1.59 ±0.058	1.59 ±0.059	1.16 ±0.097	1.33 ±0.130	0.12 ±0.006	1.49 ±0.015
E-Seam	U. Freeport	Appalachian	1.04 ±0.015	1.06 ±0.025	0.25 ±0.010	0.34 ±0.006	0.08 ±0.006	0.40 ±0.036
C-Prime	U. Kittanning	Appalachian	1.52 ±0.032	1.42 ±0.040	0.74 ±0.040	0.90 ±0.007	0.08 ±0.000	0.96 ±0.006
Mathies	Pittsburg	Appalachian	1.60 ±0.020	1.52 ±0.075	0.57 ±0.026	0.66 ±0.006	0.47 ±0.021	1.20 ±0.010
Lucas	M. Kittanning	Appalachian	1.70 ±0.025	1.69 ±0.044	0.67 ±0.006	0.82 ±0.006	0.44 ±0.006	1.19 ±0.011
Muskingum	Meiggs Creek #9	Appalachian	5.71 ±0.051	5.62 ±0.061	1.87 ±0.066	2.42 ±0.040	1.22 ±0.092	3.33 ±0.040
Tailings from Central Ohio Coal Co.	Meiggs Creek #9	Appalachian	3.28 ±0.035	3.31 ±0.096	1.87 ±0.074	1.92 ±0.170	0.02 ±0.000	2.52 ±0.035
		Pooled Std. Dev.	±0.034	±0.058	±0.051	±0.072	±0.030	±0.023

[1] Extraction performed by ASTM D2492; both analysis were performed on same solution.

[2] The proposed ASTM Atomic Absorption procedure was used.

[3] ASTM D2492.

TABLE 17. TOTAL INORGANIC SULFUR COMPARISON[1]

Coal	ASTM Titration[2]	ASTM AA[3]	TRW Plasma
Old Ben #21	0.40	0.56	0.71
Old Ben #26	0.81	0.93	1.25
Inland Peabody	1.32	1.41	1.59
Martinka	1.28	1.45	1.49
E-Seam	0.33	0.42	0.40
C-Prime	0.82	0.98	0.96
Mathies	1.04	1.13	1.20
Lucas	1.11	1.26	1.19
Muskingum	3.09	3.64	3.33
Tailings from Central Ohio Coal Co.	1.89	1.94	2.52
Pooled Standard Deviation	±0.059	±0.078	±0.023

1. Sum of sulfate and pyritic sulfur for the ASTM methods and determined directly in the plasma ashing method.

2. ASTM sulfate sulfur plus pyritic sulfur determined by titration of pyritic iron.

3. ASTM sulfate sulfur plus pyritic sulfur determined by the proposed ASTM procedure for determination of iron by atomic absorption.

TABLE 18. ORGANIC SULFUR

Coal	ASTM		TRW
	Titration	AA	Plasma
Old Ben #21	0.71	0.55	0.40
Old Ben #26	1.45	1.33	1.01
Inland Peabody	1.92	1.83	1.65
Martinka	0.31	0.14	0.10
E-Seam	0.71	0.62	0.64
C-Prime	0.70	0.54	0.56
Mathies	0.56	0.47	0.40
Lucas	0.59	0.44	0.51
Muskingum	2.62	2.07	2.38
Tailings from Central Ohio Coal Co.	1.39	1.34	0.76
Pooled Standard Deviation	±0.058	±0.085	±0.041

precise. The principal deviations in the TRW method are the use of the less sensitive iron line at 244.0 nm and the omission of lanthanum as a background suppressant. These analyses, performed in triplicate, are presented in Table 19. The following observations can be made upon examining this table.

- Sulfate sulfur values are comparable between methods for the Appalachian coals. (The single exception is the tailings sample.) The eastern interior coals all exhibit a higher sulfate content using the plasma procedure. From these results it appears that not only is frambodial pyrite difficult to extract using the ASTM procedure applied to whole coal but also the frambodial sulfate equivalent.

- Plasma ash pyritic sulfur was determined using a TRW atomic absorption iron procedure which is substantially different than the ASTM procedure. The pooled standard deviation of the TRW procedure was calculated at ±0.021 as compared to ±0.068 for the ASTM procedure. This shows a substantial improvement in precision over the ASTM procedure.

- Comparison of pyritic sulfur values is seen to follow the postulated trend with the Eastern interior coals (with the exception of Old Ben #21) exhibiting a higher plasma pyritic content than the ASTM values. Four of the Appalachian coals show excellent agreement in pyritic sulfur comparison. The Martinka, Lucas and Muskingum coals show some deviation from expected values. The reason for this poor comparison is unknown.

- The last three columns of Table 19 compare the total inorganic sulfur values from each of the three techniques used. Comparison of these values shows the expected trend, i.e., high total inorganic values for Eastern Interior coals using the plasma procedures and agreement in values for Appalachian coals (except the tailings sample). A least squares linear regression analysis was performed to compare the total inorganic values obtained using the two plasma procedures. This results in a correlation coefficient of 0.992, a slope of 1.03 and an intercept of -0.028 showing the excellent agreement between the two methods.

- The double analysis required for inorganic speciation results in a change in precision from ±0.023 to ±0.042. Thus, the most precise value for organic sulfur is obtained when a single total inorganic sulfur analysis is used.

TABLE 19. COMPARISON OF INORGANIC SPECIATION METHODS

Coal	Sulfate Sulfur		Pyritic Sulfur (AA)		Total Inorganic Sulfur		
	ASTM	Plasma	ASTM$^{(AA)}$	Plasma	ASTM[1]	Plasma[2]	Plasma[1]
Old Ben 21	0.08 ±0.000	0.22 ±0.015	0.48 ±0.066	0.41 ±0.013	0.56	0.71 ±0.011	0.63
Old Ben 26	0.16 ±0.006	0.29 ±0.064	0.77 ±0.000	0.91 ±0.010	0.93	1.25 ±0.015	1.20
Inland Peabody	0.38 ±0.012	0.53 ±0.074	1.03 ±0.006	1.17 ±0.024	1.41	1.59 ±0.015	1.70
Martinka	0.12 ±0.006	0.23 ±0.002	1.33 ±0.130	1.12 ±0.002	1.45	1.49 ±0.015	1.35
E-Seam	0.08 ±0.006	0.10 ±0.006	0.38 ±0.006	0.27 ±0.004	0.42	0.40 ±0.036	0.37
C-Prime	0.08 ±0.000	0.16 ±0.009	0.90 ±0.007	0.87 ±0.017	0.98	0.96 ±0.006	1.03
Mathies	0.47 ±0.021	0.59 ±0.028	0.66 ±0.006	0.57 ±0.011	1.13	1.20 ±0.010	1.16
Lucas	0.44 ±0.006	0.47 ±0.013	0.82 ±0.006	0.96 ±0.040	1.26	1.19 ±0.011	1.43
Muskingum	1.22 ±0.092	1.25 ±0.040	2.42 ±0.040	2.20 ±0.041	3.64	3.33 ±0.040	3.45
Tailings	0.02 ±0.010	0.44 ±0.020	1.92 ±0.170	2.04 ±0.000	1.94	2.52 ±0.035	2.48
Pooled Std. Dev.	±0.030	±0.036	±0.068	±0.021	±0.078	±0.023	±0.042

[1] Sum of sulfate and pyritic sulfur

[2] HNO_3 extraction and gravimetric sulfate

Sulfur Speciation in Liquified Coal Samples --

The present state of the art for coal analysis is seriously deficient for the sulfur forms analysis of samples in which the coal matrix has been altered significantly. This includes coke, gasified or partially gasified coal, and liquified coal samples. The problem lies in the fact that the ASTM procedure relies on the assumption that the inorganic sulfur species can be extracted from the surface or by penetration of the acid into the coal pores. Thus, anything that changes the coal structure significantly alters the basis for this assumption. Liquified coal is the worst case because coal is changed into a liquid and as a result the inorganic species are coated with a hydrophobic liquid. The plasma ashing procedure avoids this problem by removing the organic matrix before any analysis is attempted. In the experiments listed below no inorganic speciation was attempted because the inorganic sulfur was expected to be very low and the conditions under which the product was produced were expected to convert all inorganic sulfur into iron sulfide, FeS.

Four liquified coal samples obtained from Sandia Corp. of Albuquerque, New Mexico, were analyzed for total, inorganic, and organic (by difference) sulfur content using the oxygen plasma analytical procedure, with a slight modification to minimize frothing of volatile components of these samples. The results summarized in Table 20 show that in addition to removal of inorganic sulfur by filtration, substantial additional sulfur was removed in the 430°C filtered runs. The Illinois No. 6 results show that this method is capable of a high degree of precision, while the poor precision on the Kentucky No. 11 results probably indicates a degree of nonhomogeneity in the sample as the result of settling. It should be noted that this analysis indicates that both forms of sulfur varied under the experimental conditions employed. The form of sulfur that changes the most can be very important from an engineering point of view in order to avoid an expensive design modification that may not be appropriate. This type of information is not presently available from ASTM or other procedures.

Direct Organic Sulfur Determination by Plasma Ashing and SO_x Sorption--

One of the objectives of this task was to investigate the feasibility of determining organic sulfur directly. Development of such a system would be advantageous in that (1) a direct sulfur mass balance would be possible,

TABLE 20. SULFUR FORMS ANALYSIS OF LIQUIFIED COAL

Sample Description	Sulfur Analysis, % w/w			Ash Content
	Total[1]	Total Inorganic[2]	Organic (by difference)	
Illinois No. 6				
Filtered	0.52 ±0.010	0.02 ±0.007	0.50 ±0.012	2.9, 2.6
Unfiltered	0.75 ±0.023	0.10 ±0.014	0.65 ±0.027	6.2, 9.0
Kentucky No. 11				
Filtered	0.67 ±0.112	0.02 ±0.014	0.65 ±0.187	3.6, 5.7
Unfiltered	1.11 ±0.136	0.06 ±0.021	1.05 ±0.138	5.4, 7.6

[1] Average triplicate determinations

[2] Average of duplicates

[3] Runs done at 430°C

[4] Runs done at 410°C

(2) the necessity of performing an Eschka total sulfur and inorganic sulfur analysis would be eliminated, (3) direct determination would eliminate all the cumulative extraction and analysis errors, increasing the precision and accuracy of the analysis, and (4) if all four sulfur analyses (total, sulfate, pyritic, and organic) were performed directly, an error analysis of the individual analysis would be possible.

The experimentation was based on the fact that organo sulfur compounds contained in the coal matrix are converted into SO_x during the oxygen plasma decomposition. The preferred way of measurement is the use of solid sorbent because of the time for decomposition, vacuum conditions, and presence of oxygen and ozone in the exit gases. Based on data in current literature, Na_xCO_3, $NaHCO_3$, NH_4CO_3, KOH, CaO and $KMnO_4$ deposited on silica gel and molecular sieve 13x were selected for evaluation.

The results of 20 experimental runs are shown in Table 21. In all the experiments, 17 to 41 percent of the added SO_2 was found retained within the reactor chamber of the plasma asher. Because of the physical configuration of the instrument, not all of the internal surfaces could be cleaned; therefore, the reported total values could be low by an unknown and possibly varying amount. The sorption of SO_x species on the chamber walls was unexpected and the mechanism is unexplained at this time. It is felt that the problem can be circumvented. Using a different reactor design in smaller removable chambers (for ease of cleaning) and placing the sorbent canisters either within or directly behind the reactor chambers would eliminate sorption sites which cannot be cleaned without completely dismantling the instrument. As redesign and fabrication were outside the scope of the task, further experimentation was discontinued.

2.8.4 Conclusions and Recommendations

Conclusions--

A new technique for sulfur forms analysis has been developed in response to a long term need by the coal cleaning community for a more accurate and precise procedure. In this method, low temperature oxygen plasma ashing is used to selectively remove the organic matrix so that inorganic sulfur can be extracted and analyzed without interferences associated with the organic matrix. The inorganic sulfur can be analyzed

TABLE 21. EVALUATION OF SOLID SORBENTS FOR SO_x SORPTION UNDER PLASMA CONDITIONS

Sorbent System (mM)				% Recovery		
Test Number	Temperature	$KMnO_4$	KOH	Reactor Chamber	Sorbent	Total
1	25°C	-	13	30	15	45
2	25°C	12	-	13	32	45
3	25°C	6	6	41	14	55
4	25°C	6	-	23	67	90
5	25°C	-	26	23	40	63
6	100°C	4	4	13	21	34
7	100°C	4	-	24	23	47
8	100°C	10	-	28	20	48
9	100°C	-	9	17	23	40
10	25°C	13X mole sieve 16/30 mesh		21	42	63
11	25°C	13X mole sieve 30/50 mesh		17	71	88
12	25°C	13X mole sieve 30/50 mesh rerun		21	87	108

(Continued)

TABLE 21. (Continued)

Sorbent System mM						% Recovery		
Test Number	Temperature °C	$KMnO_4$	NaOH	NH_4VO_3	CaO	Reactor Chamber	Sorbent	Total
13	25	6	10	-	-	34	10	44
14	25	3	10	-	--	37	14	51
15	25	-	-	-	148	36	18	54
16	100	-	-	-	167	23	39	62
17	25	-	10	-	-	33	15	48
18	25	-	-	5	-	20	6	26
19	100	-	-	5	-	41	18	59
20	25	Activated Silica Gel Double Trap 40/80 mesh				36*	15*	51*

*Total of both traps

for sulfur forms by a modified ASTM technique or total inorganic sulfur by a highly accurate $BaSO_4$ gravimetric procedure. Specific findings are listed below.

- Plasma ashing is greater than 99% specific to the organic matrix as shown by separate oxidation studies on FeS_2(pyrite), FeS, PbS, and ZnS. The converted sulfide minerals are oxidized to sulfate. Thus, sulfur does not leave the system.
- Alkaline components such as $CaCO_3$ or CaO do not retain organic sulfur even when present at the 6% w/w level.
- The presence of iron and large amounts of nitrate does not interfere with the $BaSO_4$ procedure for total inorganic sulfur. The standard procedure to remove these possible interferences results in reduced recoveries and an increase in the variance.
- The pH in the $BaSO_4$ precipitation must be adjusted to 1 to avoid excessive solubilization of $BaSO_4$. A pH greater than 1 can result in the precipitation of iron in certain cases.
- Sulfur forms analysis can be made on liquified coal which cannot be analyzed by the ASTM procedure.

A detailed examination of the precision and accuracy of the proposed method with the ASTM D2492, the proposed ASTM atomic absorption (AA) modification to D2492, the TRW AA method, the Leco combustion method for total sulfur, and the new plasma ashing method has shown that:

- Total inorganic sulfur can be determined with a precision of ±0.02% as compared to ±0.05-0.08% for the ASTM procedure.
- The precision for proposed ASTM AA modifications of the ASTM D2492 for pyritic iron is 0.06-0.7% as compared to 0.01-0.02% for the TRW-AA procedure. The TRW method uses a less sensitime iron line and includes background correction rather than background suppressing additives.
- The Leco combustion method gives results equivalent to the Eschka method but with a reduction in precision from ±0.02-0.03% to ±0.06%.
- Discrepancies between the actual values obtained by the ASTM method and the plasma ashing method have been resolved in favor of the plasma ashing method.
- Agreement between the ASTM-AA method and expecially the ASTM-TRW-AA method is generally better than with the ASTM D2492.

The feasibility of a direct organic sulfur analysis by plasma oxidation with subsequent trapping of the organic SO_x species on solid sorbents placed in the exit port of the plasma reaction chamber has also been demonstrated.

Recommendations --

The following recommendations are made:

- The oxygen plasma coal sulfur forms analysis procedure should be further tested under round robin conditions to determine variability between laboratories.
- A larger cross section of coal regions and seams should be analyzed in replicate with results compared to ASTM D2492.
- Additional liquified coal samples, and samples obtained from other types of coal desulfurization systems should be analyzed by both the plasma and ASTM procedure (where applicable) and results compared.
- A separate program should be initiated to develop the direct determination of organic sulfur using the plasma technique and the concept of solid sorbents. The effort should be scoped to include hardware as well as methods development/optimization and also investigation of other organically bound species such as nitrogen and halogens.

2.9 TASK 12 CONTINUOUS FLOW IMPACTOR

2.9.1 Objective

The purpose of the task was to determine the feasibility of an impactor in which the collection "surface" is the interface between two opposing jets. The concept was first suggested by TRW in the "Particulate Sampling and Support" proposal to PMB in 1975.

2.9.2 Approach

When the task started, the concept was solely that — a concept. No analytical or experimental work had been done to determine feasibility. The task was initiated with a brief literature search and analytical effort to determine a key property of the device — stability of the interface between two impinging jets. When evidence of good stability properties was found, we proceeded with design, construction, and testing of a laboratory instrument. Results of the test work were positive, showing separation efficiencies similar to commercially available impactors. A draft final report was then issued.

2.9.3 Technical Discussion

All of the primary task objectives were accomplished. Test hardware was fabricated after an initial literature search indicated feasibility of the concept. Particle separation testing showed good correlation between the calculated and measured 50 percent cutoff points, which showed that the device is functionally similar to a standard impactor. Preliminary design work showed that it will be reasonable to integrate multistage hardware into a probe capable of being inserted through a standard four-inch pipe nipple, with an optical monitoring subsystem on each of five output streams. Important questions to be answered during further development deal with instrument accuracy, cost, reliability, and handling characteristics. Basic proof-of-principle, including demonstration of a field acceptable hardware concept, has been accomplished.

Luna's work was very helpful in providing a basic understanding of the stability of impinging gas jets. Because of the projected use for the continuous flow impactor, process stream sampling, our hardware configuration differed significantly from Luna's. It was one of these differences — lack of active control over the individual inlet flowrates, which was the source of the major flow instability observed early in the test program. This instability was the single largest surprise received during testing, although the probability of its occurrence is obvious in retrospect.

Particle separation testing went smoothly once all the equipment was put in working order and the test setup was finalized. There was a significant schedule loss due to failure of the first particle counter use — all data were taken using a second counter. The particle generator operation was consistent and reasonably trouble free. The main difficulty associated with its use was a need to change solution strengths relatively often to cover a range of particle sizes.

The separation test data are considered good for a first effort on a new type of device. Explanations of data trends suggest that the actual performance of the device was better than the test data show, due to less than optimum placement of the sampling tube. If subsequent testing shows this to be the case, as we believe it will, then the continuous flow impactor will have performance capabilities, in terms of sharpness of cutoff, at least comparable to presently available staged impactors. This capability, in addition to the basic advantage of continuous operation, make the device well worthy of further development.

The final subtask was a brief study to ensure that the instrument could be packaged for in situ monitoring, and to investigate the use of optical techniques to monitor the output streams. Based primarily on laboratory test data, the current opinion is that packaging impactor modules and optics in a probe to fit a standard four-inch pipe nipple will not present a problem, nor will it have a notably adverse affect on accuracy. Loss of accuracy during extraction process would likely be greater than that which will occur due to compromises required to obtain an in situ instrument.

The next step in instrument development should be a very brief test program to confirm the current thoughts on instrument performance. This would consist of such tasks as oxygen analyzer testing plus a small amount of particle separation testing with proper placement of the sampling tube. This testing should be followed by a demonstration of the optical subsystem, which could be done mainly with available in-house components. The following stage would be development of a field usable prototype. The simplicity of the continuous flow impactor components and assembly, its coordination of many of the attractive features of traditional impactors and optical particle counters while avoiding their primary drawbacks, and its potential usefulness as a diagnostic and monitoring tool, all strongly recommend that the effort begun during this task should be continued.

2.9.4 Summary and Recommendations

Within the scope of the current program, the next logical step is to perform a small amount of laboratory testing to confirm that the present thoughts on instrument operation are correct, and to obtain proper calibration data. This should be followed by construction of an in-situ two-stage device with collection on filters to verify the design of a field unit and to demonstrate acceptable operation of a staged unit. We can then proceed with development of the more complex optical system for the continuous monitoring configuration in a future contract.

It was concluded that:

- The concept of using two impinging jets for the purpose of inertial particle separation has been shown to be technically viable.
- In addition, preliminary design studies indicate that a staged impactor can easily be integrated into a sampling probe to perform in situ particulate size distribution measurements.
- Feasibility of a simple optical system compatible with the in situ sampling hardware has been shown analytically.
- The continous flow impactor has a potentially greater accuracy capability than standard impactors since it inherently avoids the traditional problems of particle bounce and reentrainment.

- Potential applications for the continuous flow impactor include control device evaluation, continuous monitoring of particulate emission for regulatory purposes, and collection of particles in an inert atmosphere to quench chemical reactions.
- A basic understanding of these continuous flow impactor operational characteristics has been attained. This can serve as a background for development of a commercially viable instrument.

Based on these findings TRW recommends that:

- All small test programs should be carried out using the existing laboratory test unit in order to fully confirm the present understanding of the device's operational characteristics.
- A second small test program should be initiated to demonstrate the selected optical monitoring technique.
- The demonstrated performance and potential usefulness of the continuous flow impactor argue strongly for development and testing of a field worthy prototype instrument. This development should be pursued.

2.10 TASK 13 UNDERSTANDING SO_3 DATA

2.10.1 Objective

The objective of this task was to develop a stack sampling procedure for the measurement of the mass emission rate of sulfur trioxide within a precision of ±10% but not to exceed ±20%.

2.10.2 Approach

This task consisted of subtasks devoted to the selection, laboratory and field testing of the SO_3 sampling train. The selection subtask consisted of a literature survey to find and evaluate potential SO_3 sampling systems. The procedures found were evaluated based on:

- Selectivity
- Sensitivity
- Accuracy
- Precision
- Ease of Operation
- Reliability

Once the candidate procedure was selected, laboratory testing was initiated.

The laboratory testing consisted of generating known streams of H_2SO_4 in the presence of varying amounts of SO_2, O_2, and H_2O. In addition, the recovery of H_2SO_4 was studied when flyash was placed on the quartz filter.

After the operation of the SO_3 sampling system was optimized in the laboratory, field tests were made at the Shawnee Test Facility in Paducah, Kentucky. These tests were conducted at the inlet and outlet of the FGD units at Paducah to determine the field utility of the equipment and procedures developed.

2.10.3 Technical Discussion

Literature Survey--

The systems used to quantify H_2SO_4 are based on selective absorption or controlled condensation. Selective absorption uses an impinger with 80%

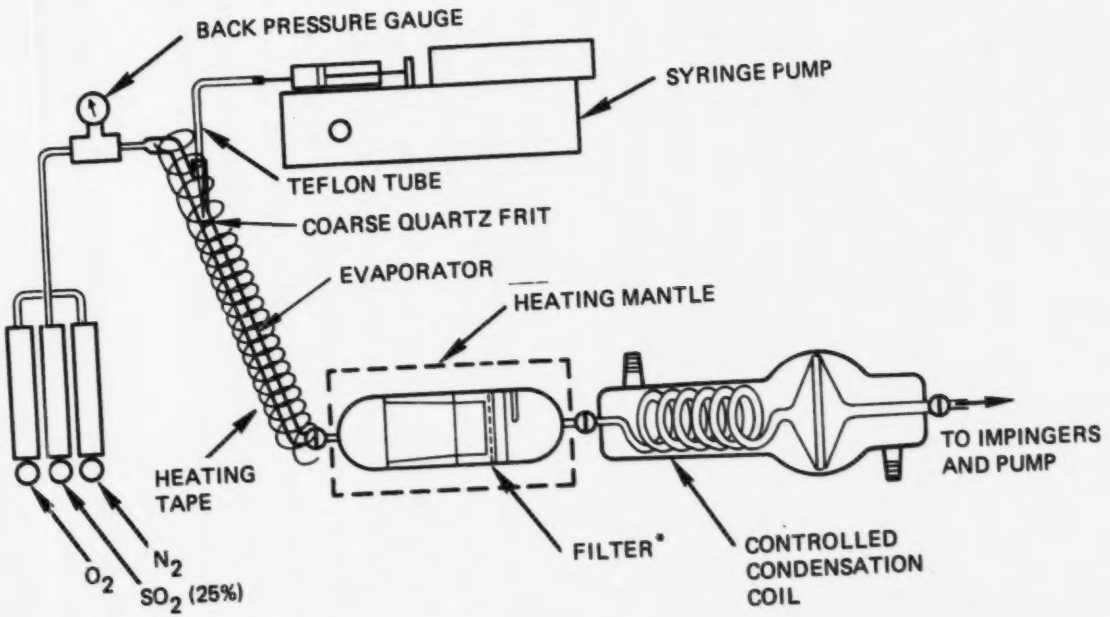
isopropyl alcohol to collect the SO_3 and to pass the SO_2. The SO_2 is collected in a back-up impinger of 3% H_2O_2. This method is currently the basis of the EPA Method 8, a compliance test for sulfuric acid mist. The major problem with this procedure is the lack of a pre-filter to effectively prevent particulate matter from reaching the IPA impinger. The particulate matter in the impinger can act either as a direct interferent by contributing $SO_4^=$ from sulfate salts, or as an indirect interferent by catalyzing the $SO_3^=$ to $SO_4^=$ oxidation in the liquid phase through action of trace elements like Fe, Cu or V.

The controlled condensation approach was first proposed by Knol (12) and has been further developed by Goksoyr and Ross (13). The Goksoyr-Ross system is the basis of an ASTM procedure for SO_x (14). In the controlled condensation approach, SO_3 is separated from the gas stream by cooling the temperature of the flue gas below the dew point for SO_3 but above the dew point of H_2O. The resulting aerosol is either collected on the walls of the cooling coil or on a back-up frit. Investigators (15, 16) studying controlled condensation in the laboratory have found the precision and accuracy to be ±6% in synthetic gas streams.

On the basis of this prior work, the controlled condensation coil was selected for additional study.

Laboratory Interference Studies --

A sulfuric acid generator based on the design of Lisle and Sensenbaugh (15) was modified and used to provide test gas streams of varying $H2SO_4$, H_2O, SO_2, O_2, and N_2. The generator was 12 mm OD quartz tube with a side arm injection port to introduce liquids onto a heated coarse quartz frit (Figure 22). The evaporator was wrapped with heating tape to vaporize solutions of H_2SO_4 that were metered into the evaporator using a syringe pump. Gas out temperatures ranged from 300°C-350°C. Adjusting the H_2SO_4 solution strength and flow produced a range of H_2SO_4 and water concentrations. The addition of the extra coarse quartz frit, ensured an even flow and evaporation of the H_2SO_4 solution. The original design tended to produce bursts of steam as the solution droplets hit the hot zone of the evaporator.



*PRELIMINARY EXPERIMENTS RAN WITH ASTM D-3226-73T QUARTZ WOOL PLUG FILTER.

Figure 22. Experimental Apparatus

The initial set of experiments sought to optimize H_2SO_4 recovery by changing the condensor temperature. In the course of these tests, information was also obtained on H_2SO_4 absorption characteristics at different temperatures. The tests showed that:

- Temperatures at or below 130°C were not adequate to prevent H_2SO_4 fallout in the probe or quartz wool section.
- Sulfuric acid collection efficiency over wide ranges of percentage moisture (4%-8%), H_2SO_4 concentration (10-20 ppm), and controlled condensation condensor (CCC) temperature (35°C-60°C) was 95% with a coefficient of variance ±6.7%.

Concurrent with the above studies, field tests of the controlled condensation system conducted under Task 2 indicated significant portions (30%) of the H_2SO_4 were being collected on the quartz wool plug placed in the probe to filter the flue gas particulate matter. At the same time, it was noted that fine particulate matter was passing through quartz wool and slowly plugging the CCC frit.

To solve these problems, an all-quartz filter holder (see Figure 23) was designed and built. The filter holder was fabricated by placing a coarse quartz frit in the female half of a standard taper joint and adding a short extension to the male joint to form a seal when a filter pad made out of Pallflex Tissuequartz was placed on the frit. Heating was accomplished using a Glass-Col heating mantle, and outlet gas temperatures were monitored with a thermocouple placed directly behind the frit. The initial system checkout showed that gas temperatures above 250°C were easily maintained. Tests were continued with this filter and it was found that:

- New filter design proved to be inert to H_2SO_4 and showed high recoveries (92% - C.V. ±3.3%) for H_2SO_4 concentrations from 1 to 28 ppm H_2SO_4.
- No H_2SO_4 was seen on filter when gas-out temperatures were above 250°C.
- Within the detection limits of the analysis scheme, no H_2SO_4 was found when SO_2 and O_2 were passed through the filter.

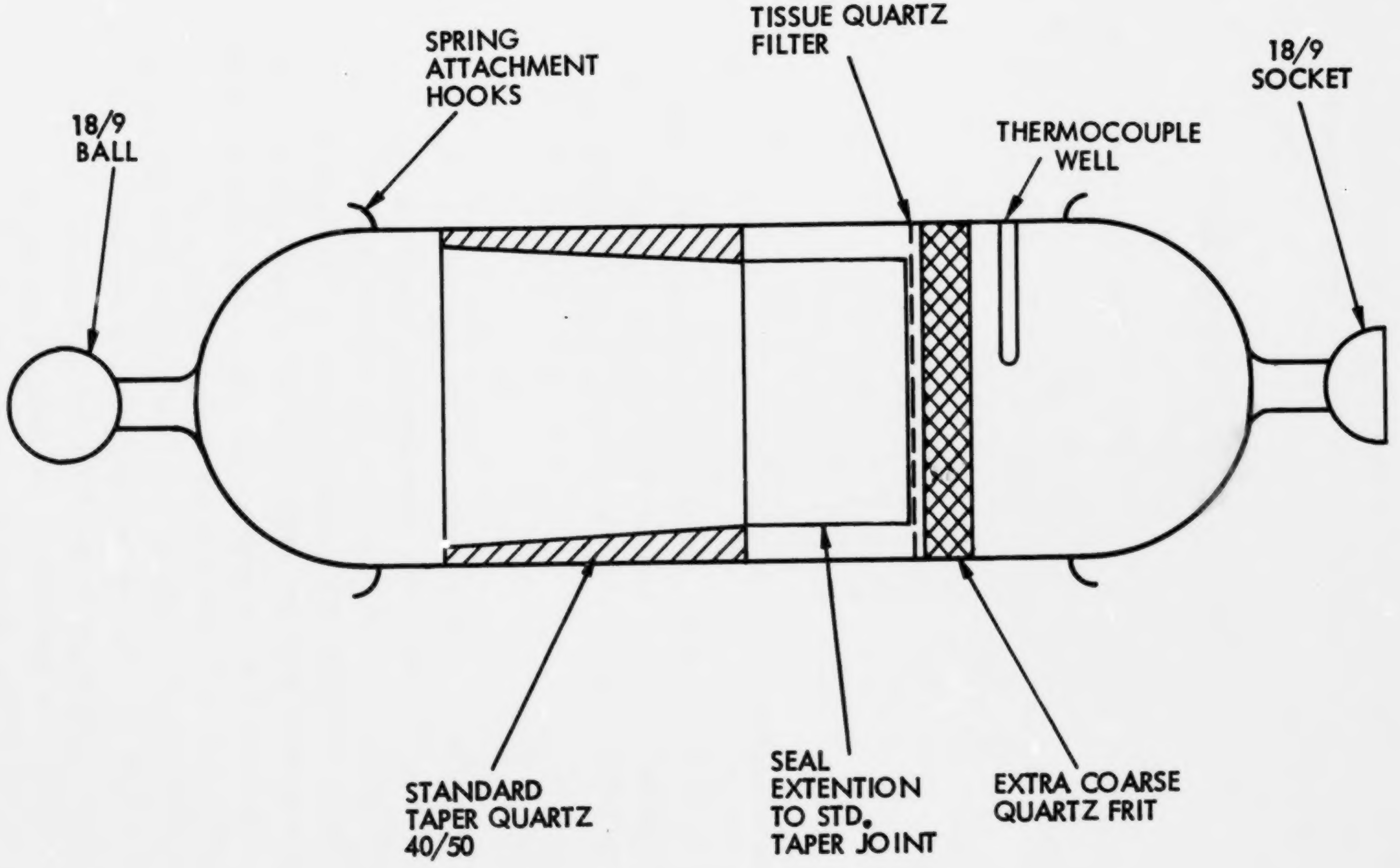


Figure 23. Quartz Filter Holder

In addition to these tests where gaseous components were varied, known amounts of flyash from the Shawnee Power Plant were placed on the quartz filter and H_2SO_4 recovery tests initiated. Table 22 summarizes the results.

TABLE 22. RESULTS OF FLYASH TESTS

Equivalent Fly Ash (g/m^3)	ppm H_2SO_4	% O_2	ppm SO_2	Percentage H_2SO_4 Found		
				Filter	CCC	Total
1.3	9	8	0	15	81	96
1.3	12	8	650	14	86	100
1.3	11	8	5300	11	87	98
0.13	11	8	700	0	89	89

As Table 22 shows, reduced amounts of H_2SO_4 were recovered in the coil, though the H_2SO_4 mass balance (obtained through titrating the flyash and expressing any alkalinity change in milliequivalents) was quite good.

Field Tests --

Extensive field trials with the CCS were conducted on a pilot FGD located at a TVA coal-fired power plant in Paducah, Kentucky. This pilot facility is a prototype Flue Gas Desulfurization (FGD) Unit utilizing wet lime or limestone SO_2 scrubbing chemistry. The feed for the unit is a slipstream taken from the number 10 boiler either prior to or after the ESP. The inlet flue gas mass particulate loadings were approximately 11.4 g/m^3, 0.17 g/m^3, and 0.06 g/m^3, depending on whether the gas was obtained directly from the boiler, from the outlet of the ESP, or from the outlet of the FGD unit, respectively. Sulfur dioxide concentrations varied from 2,000 to 4,000 ppm at the inlet and approximately 400 to 800 ppm exiting the unit. Gas temperatures and moisture percent varied from 165°C to 121°C and 8% to 17%, respectively, across the FGD unit.

The field test consisted of simultaneous inlet/outlet H_2SO_4 measurements across the FGD unit taken over a period of approximately 30 days. The average inlet H_2SO_4 value was 8.3 ppm (ranged from 0.4-24.8 ppm) while the average outlet value was 3.1 ppm (ranged from 0.0 to 13.9 ppm). The coefficient of variance was ±66.3%.

Since the inlet H_2SO_4 coefficient of variance (CV_T) represents the sum, $[(CV_T) = [(CV_S)^2 + (CV_M)^2]^{1/2}]$ of source fluctuation (CV_S) and method error (CV_M), the source fluctuation can be estimated by assigning a coefficient of variance to the field CCS. This coefficient of variance reflects errors in reading temperature and pressures, accuracy of leak rates, as well as rinsing recovery or titration errors which might affect the ultimate calculation of the H_2SO_4 concentrations. It is estimated that the field accuracy of the CCS is ±11%, and thus the coefficient of variance of the source is ±65%. This high CV_S implies that to obtain a good average H_2SO_4 value from this type of source, it will be necessary to take a large number of samples spread out over a period of days.

2.10.4 Summary of Results and Recommendations

As a result of this test program, these facts were learned about the CCS:

1) The average laboratory coefficient of variance was ±7%.

2) Oxidation of SO_2 did not occur at the recommended filter holder temperatures with 4000 ppm SO_2 and 8% O_2. Also fly ash from a coal-fired utility placed on the filter did not have a catalytic effect under those conditions.

3) When 0.3 g of fly ash equivalent to 1.3 g/m^3 was placed on the surface of the filter, the amount of H_2SO_4 recovered was reduced by $\sim$12% when a gas stream containing 10 ppm of H_2SO_4 was passed through the system.

4) There appears to be a slight difference between H_2SO_4 recovery in the presence of fly ash with and without SO_2 but with the data available at this time it is impossible to predict its exact effect.

5) The coefficient of variance of the H_2SO_4 output at the coal-fired utility tested was estimated to be ±65%.

It is recommended that additional studies be performed that will refine the current design of a controlled condensation system. Work is also necessary to develop an automated version of the controlled condensation system so that studies on the variable nature of SO_3 emissions can be related to changes in process operating conditions.

2.11 TASK 14 KVB TEST SUPPORT

2.11.1 Objective

In July 1976, KVB Engineering conducted a Level 1 sampling effort in accordance with the draft copy of the EPA-IERL Level 1 Procedures Manual, on an experimental coal-fired boiler at the KVB facility in Tustin, California. The specific objectives of this task were to support KVB by:

1) Determining the adequacy of the sampling test as a Level 1 Environmental Assessment in accordance with the draft copy of the Level 1 Procedures Manual.
2) Answering any questions from KVB which might arise concerning the requirements of the draft IERL Procedures Manual.
3) Analyzing samples in accordance with the Level 1 procedures in parallel with KVB's analytical subcontractor, Calspan.

2.11.2 Approach

Prior to the sampling activity, consultations were held with KVB to answer questions and assist in formulating the test plan. TRW personnel were also present during the boiler testing to continue the process of advising and supporting KVB. Samples taken from the coal-fired boiler control device system and all parts of the SASS train were then distributed in equal portions to Calspan and TRW Laboratories for analysis.

The sampling effort was conducted in accordance with the IERL-RTP Procedures Manual for Level 1 Environmental Assessments.

In accordance with the EPA Technical Directive, the analysis format was structured after the Level 1 procedures only where this approach was compatible with the Calspan analysis plan. Reasonable adherence to the Calspan analysis format was necessary in order to:

1) Provide a collaborative data base among KVB/TRW/Calspan, and
2) To attempt to provide a data base accurate enough to establish a ±25 percent balance closure as called for in the task technical directive.

For these reasons, strict adherence to the Level 1 analysis procedures was not observed in all cases. As required by the IERL-RTP Level 1 Procedures Manual, memoranda delineating specific Level 1 analysis deviations were submitted to EPA IERL-RTP prior to the initiation of any analysis activities.

2.11.3 Technical Discussion

During the testing, KVB's experimental boiler was fired on Pittsburgh #8 seam coal at an approximate rate of 93 kg/hr. A 30 DSCM SASS sample was collected at an average of 93 percent isokinetic. A total of 77 grams of particulate were collected in the SASS cyclones and filter, yielding ample amounts of material for the chemical analyses. Samples were also taken of the process solids (i.e., furnace slag, fire tube ash, lower stack ash, duct ash, and baghouse ash) and feed coal in order to be able to perform a mass balance. Analysis of these samples was performed according to the Level 1 procedures with the addition of specific AAS determinations for Se, Cd, Pb, and V. These elements were added to provide quantitative data points for the mass balance examination.

The final report prepared under this task examined problems encountered with Level 1 sampling and analysis procedures and presented conclusions and recommendations where appropriate. Elemental analysis results were tabulated in detail, and spark source mass spectrometry, atomic absorption, and colorimetric values were cross-referenced to provide data comparisons. Final results were presented as mass balance closures from the standpoint of both coal feed and baghouse as they relate to the SASS sample catch. Level 1 organic analyses were also performed on all samples with extended LC/LRMS tests to increase accuracy and also to aid in evaluating the procedure. Photomicrographs of the filters were presented along with general observations concerning the entrained particulate.

2.11.4 Summary of Results and Recommendations

The emphasis in the use of the data generated under this task was on the mass balance. In this regard the SASS was an effective unit performing well within the Level 1 error limits of a factor of 2-3. The cumulative percentage differences between the SSMS values and the special case analyses values for total quantities trapped in the SASS train, and for the theoretical ideals for baghouse and coal feed, all showed excellent reproducibility in terms of precision.

As with all trace element analyses, many elements could not be quantified due to detection limit levels. This inherent problem appeared, however, to be increased by the Parr bomb preparation procedure required for all Level 1 samples by the Level 1 methods. This was attributed to any one or all of the following three conditions:

1) Incomplete combustion of the samples, particularly those consisting of primarily inorganic matrices.
2) Small quantity of sample used for ashing.
3) Dilution of the Parr solution by bringing to a standard volume (100 mL) in volumetric flasks.

These reductions in analytical sample quantities could be avoided or minimized by not bombing inorganic samples (for which the combustion is unnecessary) and combining sequential combustions to provide more concentrated solutions.

Another notable conclusion of this task was that the SSMS technique is more reliable than the atomic absorption or colorimetric methods for As, Hg, Sb since in all cases concentrations were above the detection levels for SSMS, while in most cases concentrations were below the detection levels for the atomic absorption and colorimetric methods.

This study also showed that trace elements are condensed throughout the XAD-2 module. This observation resulted in the recommendation that a nitric acid rinse step should be included in the XAD-2 module sample recovery procedures.

2.12 TASK 21 TEST DATA MODELING

2.12.1 Objective

The objective of this task was to develop test (computer) models which permits a chemist to evaluate, a priori, the variation in his test results using assumptions based on his experience.

2.12.2 Approach

The computer program (see attachments) answers the following questions:

1) A chemist will take either 2 or 3 samples (replications) for a particular test. What kind of results can he expect? To evaluate his results he can input either a ± range or the actual σ along with the nominals.

   The first example, Attachment A, provides results of eleven tests of two samples each when sampling from a population with a nominal value of 45 and a σ of 1.74. For this standard deviation, the coefficient of variation is only CV = 1.74/45(100) = 3.8%. Still the scatter in percent range is quite variable.

   The second example, Attachment B, provides the same type of results except three samples per test will be analyzed. Here the nominal value is 77 and the variation was provided as a percent range of 21.8. The reported percent ranges are quite variable.

2) The chemist has three populations of known mean and standard deviation (or ± percent range) values. He wishes to know the mean and standard deviation values of a new population defined as sums of three samples, one from each of the three original populations. Replicated samples from this new population should be available to enable the chemist to examine the effect on the percent ranges (±) as a consequence of the original population specifications.

   The computer program accepts known mean and standard deviation (or ± percent range) values of the three original populations and using a pseudo-random number generator produces samples from a normal distribution based on the given parameters. The sum of one sample from each of these populations constitutes a sample of the new population. Either two or three samples per test are allowed and as many tests as desired may be requested. Both sample mean and sigma, as well as the population mean and sigma, are provided to enable the researcher to compare the samples generated with the theoretical population parameters. (See Attachment C.)

Utilizing this program the chemist is able to specify one of many sampling test plans, to examine the resulting test sampling test plans, to examine the resulting test samples, and to compare the test sample characteristics with those of the population.

3) The chemist again has three populations of known mean and standard deviation (or ± percent range) values. The populations are now comprised of the original unknown (or summation) population and any two of the three originally known populations which define the summation population. The mean and standard deviation values of the remaining third original population (presently unknown) are now required. Replicated samples for this remaining population should again be available to enable the researcher to examine the effect of the given population parameters on the percent ranges (±).

The program accepts the known mean and standard deviation values for the given populations. Using a pseudo-random number generator, samples from a normal distribution are produced based on the parameters for each of the given populations. The samples for the unknown population are produced by subtracting from a summation population sample, one sample from each of the first two populations. Either two or three samples per test are allowed and as many tests as desired may be requested. Both sample mean and sigma, as well as the population mean and sigma, are provided to enable the chemist to compare the samples generated with the theoretical population parameters. (Attachment D).

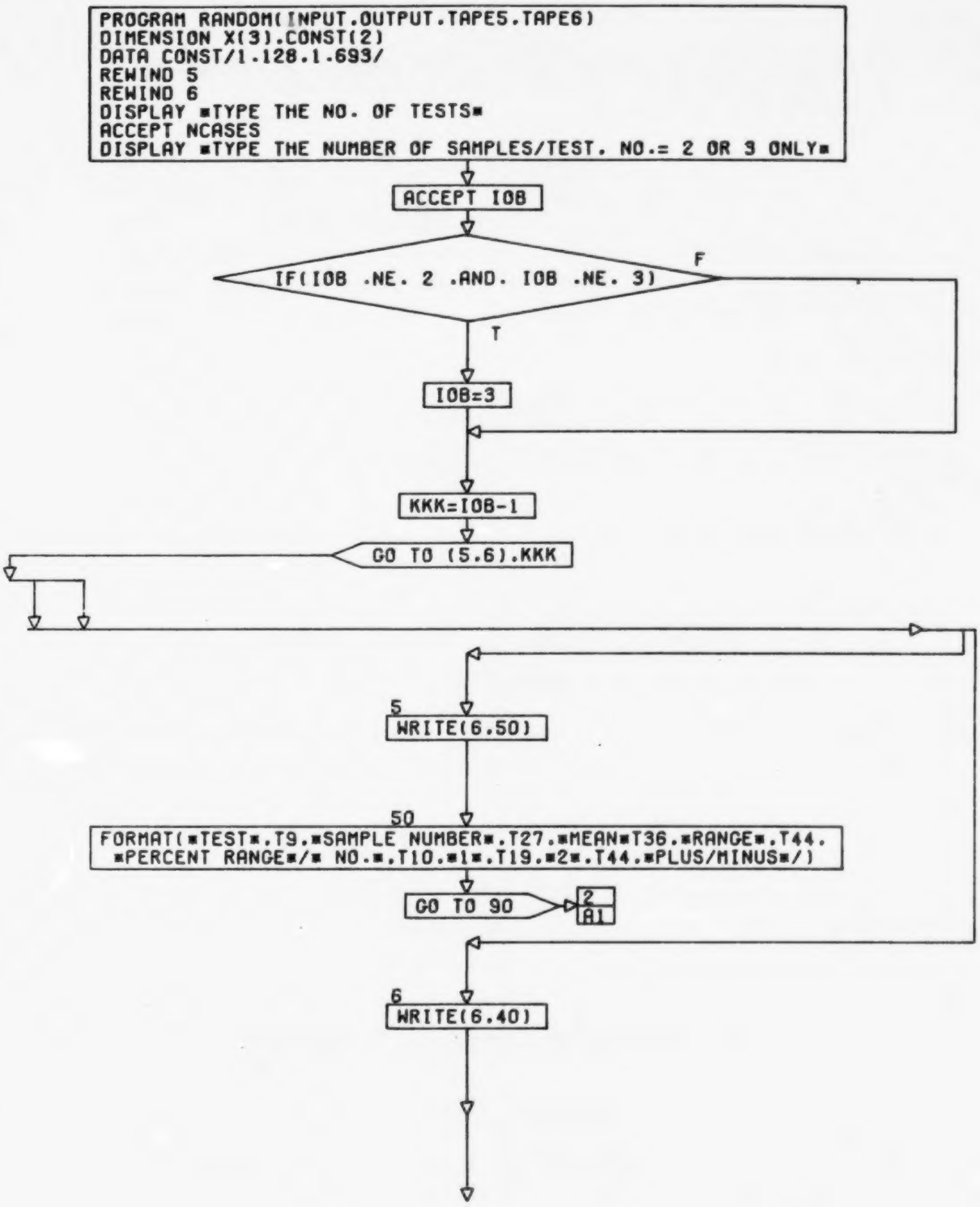
TASK 21 - LISTINGS FOR PROGRAM "ROUTINE" AND ATTACHMENTS

FUNCTIONAL OUTLINE OF PROGRAM "RANDOM"

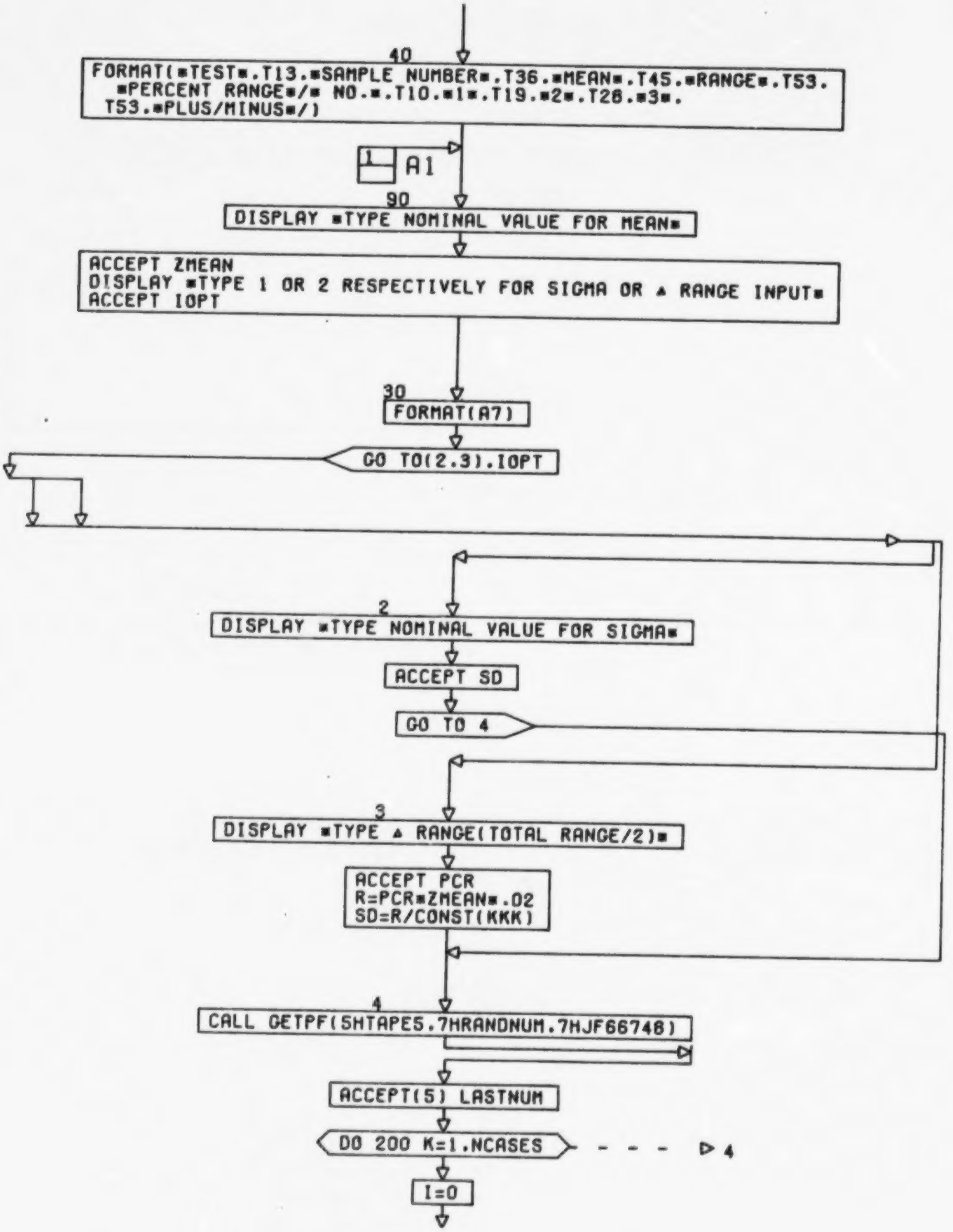
(Usage described in task 21 write-up)
(Sample outputs presented in Attachment A and B of above)

READ INPUT	a.) NUMBER OF TESTS
	b.) NUMBER OF SAMPLES/TEST, i.e., 2 OR 3
	c.) NOMINAL VALUE FOR MEAN
	d.) NOMINAL VALUE FOR SIGMA OR A PERCENT RANGE
	e.) LAST RANDOM NUMBER USED BY RANDOM NUMBER GENERATOR
FOR EACH TEST	a.) OBTAIN EITHER 2 OR 3 NORMALLY RANDOM SAMPLES FROM THE POPULATION DEFINED BY NONINAL MEAN AND SIGMA/ OR PERCENT RANGE.
	b.) CALCULATE THE MEAN, RANGE AND PERCENT RANGE (PLUS/MINUS) OF SAMPLES OBTAINED.
PRINT OUTPUT TABLE	a.) INDICATING TEST NUMBER, SAMPLES OBTAINED.
	b.) MEAN, RANGE, AND PERCENT RANGE (PLUS/MINUS) OF SAMPLES OBTAINED.

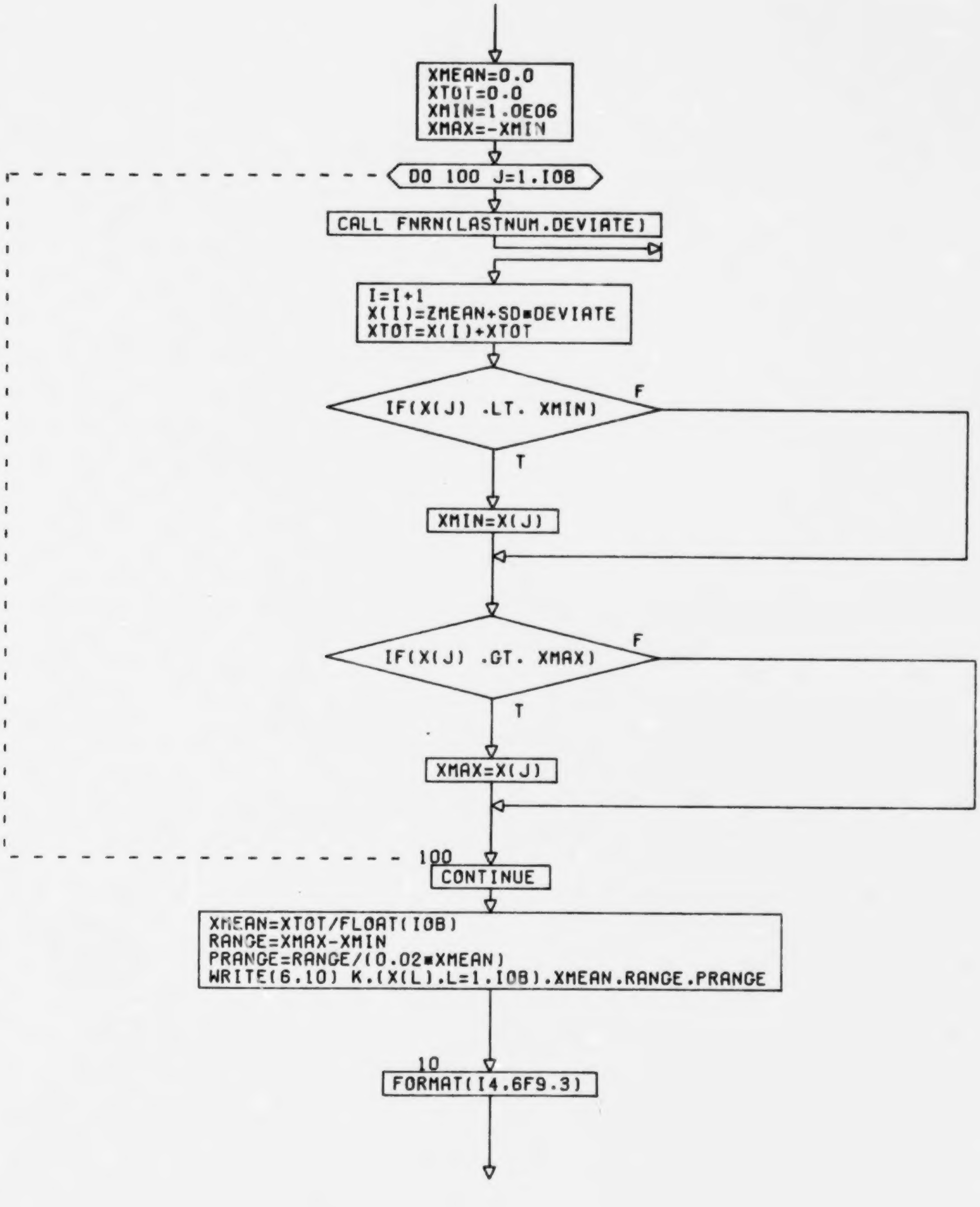
```
      PROGRAM RANDOM(INPUT,OUTPUT,TAPE5,TAPE6)
      DIMENSION X(3),CONST(2)
      DATA CONST/1.128,1.693/
      REWIND 5
      REWIND 6
      DISPLAY *TYPE THE NO. OF TESTS*
      ACCEPT NCASES
      DISPLAY *TYPE THE NUMBER OF SAMPLES/TEST, NO.= 2 OR 3 ONLY*
      ACCEPT IOB
      IF(IOB .NE. 2 .AND. IOB .NE. 3) IOB=3
      KKK=IOB-1
      GO TO (5,6),KKK
5     WRITE(6,50)
50    FORMAT(*TEST*,T9,*SAMPLE NUMBER*,T27,*MEAN*T36,*RANGE*,T44,
     ^ *PERCENT RANGE*/* NO.*,T10,*1*,T19,*2*,T44,*PLUS/MINUS*/)
      GO TO 90
6     WRITE(6,40)
40    FORMAT(*TEST*,T13,*SAMPLE NUMBER*,T36,*MEAN*,T45,*RANGE*,T53,
     ^  *PERCENT RANGE*/* NO.*,T10,*1*,T19,*2*,T23,*3*,
     ^ T53,*PLUS/MINUS*/)
90    DISPLAY *TYPE NOMINAL VALUE FOR MEAN*
      ACCEPT ZMEAN
      DISPLAY *TYPE 1 OR 2 RESPECTIVELY FOR SIGMA OR % RANGE INPUT*
      ACCEPT IOPT
30    FORMAT(A7)
      GO TO(2,3),IOPT
2     DISPLAY *TYPE NOMINAL VALUE FOR SIGMA*
      ACCEPT SD
      GO TO 4
3     DISPLAY *TYPE % RANGE(TOTAL RANGE/2)*
      ACCEPT PCR
      R=PCR*ZMEAN*.02
      SD=R/CONST(KKK)
4     CALL GETPF(5HTAPE5,7HRANDNUM,7HJF66748)
      ACCEPT(5) LASTNUM
      DO 200 K=1,NCASES
      I=0
      XMEAN=0.0
      XTOT=0.0
      XMIN=1.0E06
      XMAX=-XMIN
      DO 100 J=1,IOB
      CALL FNRN(LASTNUM,DEVIATE)
      I=I+1
      X(I)=ZMEAN+SD*DEVIATE
      XTOT=X(I)+XTOT
      IF(X(J) .LT. XMIN) XMIN=X(J)
      IF(X(J) .GT. XMAX) XMAX=X(J)
100   CONTINUE
      XMEAN=XTOT/FLOAT(IJB)
      RANGE=XMAX-XMIN
      PRANGE=RANGE/(0.02*XMEAN)
      WRITE(6,10) K,(X(L),L=1,IJB),XMEAN,RANGE,PRANGE
10    FORMAT(I4,6F9.3)
200   CONTINUE
      REWIND 5
      DISPLAY (5) LASTNUM
      REWIND 5
      CALL RPLPF(5HTAPE5,7HRANDNUM,7HJF66748)
      STOP
      END
```

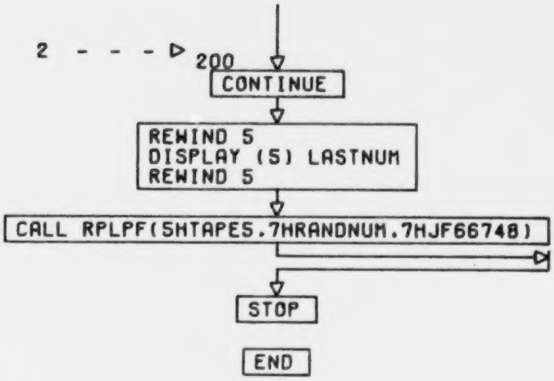


```
PROGRAM RANDOM(INPUT.OUTPUT.TAPE5.TAPE6)
DIMENSION X(3).CONST(2)
DATA CONST/1.128.1.693/
REWIND 5
REWIND 6
DISPLAY *TYPE THE NO. OF TESTS*
ACCEPT NCASES
DISPLAY *TYPE THE NUMBER OF SAMPLES/TEST. NO.= 2 OR 3 ONLY*
ACCEPT IOB
IF(IOB .NE. 2 .AND. IOB .NE. 3)
IOB=3
KKK=IOB-1
GO TO (5.6).KKK
5 WRITE(6.50)
50 FORMAT(*TEST*.T9.*SAMPLE NUMBER*.T27.*MEAN*T36.*RANGE*.T44.
 *PERCENT RANGE*/* NO.*.T10.*1*.T19.*2*.T44.*PLUS/MINUS*/)
GO TO 90
6 WRITE(6.40)
```



```
40  FORMAT(■TEST■.T13.■SAMPLE NUMBER■.T36.■MEAN■.T45.■RANGE■.T53.
      ■PERCENT RANGE■/■ NO.■.T10.■1■.T19.■2■.T28.■3■.
     T53.■PLUS/MINUS■/)
90  DISPLAY ■TYPE NOMINAL VALUE FOR MEAN■
    ACCEPT ZMEAN
    DISPLAY ■TYPE 1 OR 2 RESPECTIVELY FOR SIGMA OR ▲ RANGE INPUT■
    ACCEPT IOPT
30  FORMAT(A7)
    GO TO(2.3).IOPT
2   DISPLAY ■TYPE NOMINAL VALUE FOR SIGMA■
    ACCEPT SD
    GO TO 4
3   DISPLAY ■TYPE ▲ RANGE(TOTAL RANGE/2)■
    ACCEPT PCR
    R=PCR■ZMEAN■.02
    SD=R/CONST(KKK)
4   CALL GETPF(5HTAPE5.7HRANDNUM.7HJF66748)
    ACCEPT(5) LASTNUM
    DO 200 K=1.NCASES
    I=0
```


XMEAN=0.0
XTOT=0.0
XMIN=1.0E06
XMAX=-XMIN
DO 100 J=1.IOB
CALL FNRN(LASTNUM.DEVIATE)
I=I+1
X(I)=ZMEAN+SD*DEVIATE
XTOT=X(I)+XTOT
IF(X(J) .LT. XMIN)
F
T
XMIN=X(J)
IF(X(J) .GT. XMAX)
F
T
XMAX=X(J)
100
CONTINUE
XMEAN=XTOT/FLOAT(IOB)
RANGE=XMAX-XMIN
PRANGE=RANGE/(0.02*XMEAN)
WRITE(6.10) K.(X(L).L=1.IOB).XMEAN.RANGE.PRANGE
10
FORMAT(I4.6F9.3)


2
200
CONTINUE
REWIND 5
DISPLAY (5) LASTNUM
REWIND 5
CALL RPLPF(5HTAPES.7HRANDNUM.7HJF66748)
STOP
END

Attachment A

```
 TYPE THE NO. OF TESTS
? 11
 TYPE THE NUMBER OF SAMPLES/TEST, NO.= 2 OR 3 ONLY
? 2
 TYPE NOMINAL VALUE FOR MEAN
? 45
 TYPE 1 OR 2 RESPECTIVELY FOR SIGMA OR % RANGE INPUT
? 1
 TYPE NOMINAL VALUE FOR SIGMA
? 1.74
[ LIST,TAPE6


TEST     SAMPLE NUMBER       MEAN      RANGE    PERCENT RANGE
 NO.       1         2                          PLUS/MINUS

   1    45.237    47.013    46.125     1.776     1.925
   2    46.178    49.028    47.603     2.851     2.994
   3    44.828    46.807    45.817     1.979     2.160
   4    44.922    47.108    46.015     2.186     2.375
   5    44.721    47.003    45.862     2.282     2.488
   6    42.208    47.475    44.841     5.267     5.873
   7    45.642    44.716    45.179      .926     1.025
   8    44.395    45.915    45.155     1.520     1.683
   9    43.639    44.782    44.210     1.143     1.293
  10    45.146    45.296    45.221      .150      .166
  11    45.917    46.800    46.358      .882      .952
```

Attachment B

```
[ LGO
 TYPE THE NO. OF TESTS
? 16
 TYPE THE NUMBER OF SAMPLES/TEST, NO.= 2 OR 3 ONLY
? 3
 TYPE NOMINAL VALUE FOR MEAN
? 77
 TYPE 1 OR 2 RESPECTIVELY FOR SIGMA OR % RANGE INPUT
? 2
 TYPE % RANGE(TOTAL RANGE/2)
? 21.8
[ LIST,TAPE6


TEST          SAMPLE NUMBER            MEAN      RANGE    PERCENT RANGE
 NO.      1         2         3                           PLUS/MINUS

   1   30.989    68.073    86.691    61.918    55.701    44.980
   2   81.095    96.980    96.178    91.418    15.885     8.688
   3   64.664    93.688    82.805    80.386    29.024    18.053
   4   86.037    82.266    77.430    81.911     8.607     5.254
   5   97.182    87.578    60.589    81.783    36.593    22.372
   6   94.835    83.842    70.545    83.074    24.290    14.620
   7   60.157    82.160    49.591    63.969    32.569    25.457
   8   88.700    55.831   102.228    82.253    46.398    28.204
   9   80.615    62.766    62.595    68.658    18.020    13.123
  10   74.788    91.744   100.202    88.911    25.414    14.292
  11  104.579    76.514    78.429    86.508    28.065    16.221
  12   96.400    77.160    59.348    77.636    37.052    23.862
  13   83.083    58.523    56.503    66.036    26.580    20.126
  14   78.896    37.946    95.892    70.911    57.945    40.858
  15   81.821   111.168    77.536    90.175    33.631    18.648
  16   49.072    69.912    73.529    64.171    24.457    19.056
```

Attachment C

```
RX,I=GRPRAN,G
 TYPE 1 FOR TOTAL POPULATION SOLN.
 TYPE 2 FOR INDIV POPULATION SOLN.
? 1
 ORDER REQUIRED PARAMETERS P(1),P(2),P(3),P(TOTAL)
 OMITTING THE UNKNOWN PARAMETER

 TYPE THE NO. OF TESTS
? 14
 TYPE THE NUMBER OF SAMPLES/TEST, NO.= 2 OR 3 ONLY
? 3
 TYPE NOMINAL VALUES FOR MEAN
? 12,23.1,17.4
 TYPE 1 OR 2 RESPECTIVELY FOR SIGMA OR % RANGE INPUT
? 1
 TYPE NOMINAL VALUES FOR SIGMA
? 1,2,3
[ LIST,TAPE6

TEST        SAMPLE NUMBER              MEAN      RANGE    PERCENT RANGE
 NO.     1          2          3                          PLUS/MINUS

   1    45.859    54.412    59.105    53.125    13.246    12.467
   2    49.719    52.700    44.802    49.074     7.897     8.046
   3    58.759    51.586    49.905    53.417     8.854     8.288
   4    56.751    54.939    48.775    53.489     7.976     7.456
   5    51.552    53.502    52.591    52.548     1.950     1.855
   6    51.483    53.869    53.470    52.941     2.386     2.254
   7    59.491    56.794    44.645    53.644    14.846    13.837
   8    51.569    50.679    54.079    52.109     3.399     3.262
   9    56.279    51.292    57.898    55.156     6.607     5.989
  10    50.899    50.734    56.544    52.726     5.811     5.510
  11    49.421    55.193    57.264    53.959     7.842     7.267
  12    52.852    56.884    50.849    53.528     6.035     5.638
  13    51.055    50.079    61.706    54.280    11.627    10.710
  14    50.634    51.118    46.262    49.338     4.856     4.921

SAMPLE MEAN  =   52.810          POPULATION MEAN  =   52.500
SAMPLE SIGMA =    3.79           POPULATION SIGMA =    3.74

[
```

Attachment D

```
LGO
 TYPE 1 FOR TOTAL POPULATION SOLN.
 TYPE 2 FOR INDIV POPULATION SOLN.
? 2
 ORDER REQUIRED PARAMETERS P(1),P(2),P(3),P(TOTAL)
 OMITTING THE UNKNOWN PARAMETER

 TYPE THE NO. OF TESTS
? 14
 TYPE THE NUMBER OF SAMPLES/TEST, NO.= 2 OR 3 ONLY
? 3
 TYPE NOMINAL VALUES FOR MEAN
? 12,23.1,52.5
 TYPE 1 OR 2 RESPECTIVELY FOR SIGMA OR % RANGE INPUT
? 1
 TYPE NOMINAL VALUES FOR SIGMA
? 1,2,3.7
[ LSST,
↑ LIST,TAPE6


TEST          SAMPLE NUMBER                MEAN       RANGE    PERCENT RANGE
 NO.      1          2          3                               PLUS/MINUS

   1   17.587     20.360     25.360      21.102       7.774     18.419
   2   11.753     22.133     17.338      17.075      10.379     30.394
   3   17.136     18.899     15.564      17.200       3.335      9.696
   4   24.363     21.794     19.352      21.836       5.011     11.474
   5   14.679     20.497     10.357      15.178      10.139     33.402
   6   19.852     27.115     10.892      19.286      16.223     42.059
   7   17.622      9.156     16.554      14.444       8.467     29.309
   8   20.251     17.461     19.748      19.153       2.790      7.284
   9   14.418     21.207      7.305      14.310      13.902     48.575
  10   10.475     18.585     15.706      14.922       8.110     27.174
  11   18.174     15.971     12.502      15.549       5.672     18.240
  12   13.702     12.206      5.397      10.435       8.306     39.798
  13   15.557     12.461     20.601      16.206       8.140     25.113
  14   20.567      9.255     18.723      16.182      11.311     34.950

SAMPLE MEAN  =    16.634              POPULATION MEAN  =    17.400
SAMPLE SIGMA =     4.72               POPULATION SIGMA =     4.32

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2.13 TASK 22 EVALUATION OF DRY SORBENTS AND FABRIC FILTRATION FOR FGD

2.13.1 Objective

In 1976 the use of dry sorbents in a baghouse for treating exhaust from a flue gas desulfurization unit (FGD) was examined by TRW for EPA and by Bechtel Corporation for the Electric Power Research Institute (EPRI). Both studies concluded that, based on available information, the dry sorbent/baghouse FGD concept held considerable promise of economic advantage under certain geographic, process and regulatory constraints. The optimistic view of the concept, however, must be tempered by the fact that experimental data were sketchy, certain major institutional and financial barriers existed, and, most significantly, the available cost estimates were prepared and presented by firms having a potential financial benefit in the eventual commercialization of the process.

In order to further evaluate the concept prior to embarking on expensive field test work, EPA requested that TRW conduct a more thorough study to include independent assessment of sorbent costs, system capital costs, system operating costs and disposal costs. The basic objective of this study was to determine whether or not the apparent economic advantage exhibited by the concept remains intact after independent, third-party evaluation and whether the economic (and other) advantages are sufficiently large to warrant further development of the process.

2.13.2 Approach

The goal was to estimate costs and evaluate problems associated with a typical commercial utility dry sorbent/baghouse FGD system. By estimating costs using a situation which approximates a "best case" and comparing these costs with a currently available FGD system, it was possible to determine if the dry sorbent/baghouse FGD process represents a substantial breakthrough in FGD technology and can be expected to attain substantial market penetration in the future.

"Best case" conditions were selected after examination of: current trends in boiler design, coal supplies in the vicinity of potential sorbent supplies, SO_2 removal requirements, and available experimental data on dry sorbent performance. The conditions that were selected for detailed economic evaluation were:

- A new 500 MW boiler
- 1% sulfur western coal
- 750 mile (1,200 km) distance from nahcolite supplies
- Semi-arid region with the water table 50 feet (15 m) below the surface
- 400°F Baghouse temperature
- 70% SO_2 removal required.

Although additional refinement of conditions may produce a slightly lower cost base-case for this study, any conditions which are site specific or narrow in application would be unrealistic since the equivalent of ten 500 MW installations would be required to support one commercial-scale nahcolite mine. This is approximately 4% of the power output of the committed fossil-fueled generating plants for the period 1977-1986.

2.13.3 Technical Discussion

Published experimental data indicate that nahcolite (impure $NaHCO_3$) is the most promising sorbent for use in the dry sorbent baghouse flue gas desulfurization (FGD) concept. Available data are adequate for cost estimation that is on the order of -20 percent to +50 percent accurate. These data are not, however, sufficient to permit potential users (electric utility companies) to accept commercial bids with confidence. A recent and rather extensive pilot test conducted by Wheelabrator-Frye, Inc., Superior Oil Co., and a midwestern utility consortium may well provide sufficient data upon which to base a commercial design. The extent to which these data will be made public is not known at this time.

The reserves of nahcolite are adequate to supply even very extensive application of the dry sorbent/baghouse FGD concept to western and midwestern low sulfur coal-fired boilers. The material is not currently mined. A reasonable commercial price for nahcolite (70 percent assay) is $25 per ton at the mine mouth and $32.50 per ton at a power plant located approximately 750 miles (1,200 kilometers) from the mine site (northwestern Colorado). IRI and Superior Oil have confirmed that a firm commitment for supplying nahcolite to several large baghouse FGD installations would be necessary before any of the three nahcolite lease holders would be able to invest the significant sums of money required to open a nahcolite production mine.

The wastes generated by a 500 MW application of the dry sorbent/baghouse FGD process can be disposed of in an environmentally acceptable manner. The basic disposal concept involves a landfill designed specifically to preclude groundwater, surface water and rainfall from entering the deposit of soluble waste material. The prevention of groundwater intrusion is accomplished through careful site selection and exclusion of surface water and rainfall by combination of dikes and an impermeable (butyl rubber) membrane placed over the landfill site. Landfill costs for the concept and design described in this report are estimated at $6 per ton of waste.

The dry sorbent/baghouse FGD process, when costed in the base case selected for analysis in this study, shows capital costs of $46 per KW and an annualized operating cost of 2.60 mills per kWh. This is 35% lower than the base case limestone FGD process using those inputs which give a flue gas composition of 4.3×10^6 lb/hr flow, 36,500 lb/hr ash, 8.17×10^3 lb/hr SO_2 and 3.8×10^5 lb/hr moisture, equivalent to the nahcolite/baghouse FGD system. The TVA cost estimates were computed to be $119 per KW and 4.08 mills per kWh for the capital costs and annualized operating costs, respectively. Even in view of the accuracy of the cost estimating methods (-20% to +50%), the cost differences between the dry sorbent/baghouse FGD system and the limestone scrubbing FGD process must be considered promising. This, in conjunction with the fact that the limestone scrubber is considered one of the more economical of flue gas desulfurization schemes, makes the dry sorbent/baghouse system seem quite favorable.

However, since the proposed concept is extremely sensitive to the amount of sulfur removed (more than 40 percent of the annualized operating costs for the dry sorbent/baghouse system is for sorbent and waste disposal compared with 3% for the limestone scrubbing process), applications to high sulfur coal-firing may not be economically competitive with the limestone scrubber.

Experimental data indicate that nahcolite utilization may approach 100% if the dry sorbent baghouse is operated at about 525°F (274°C). This potential improvement in utilization would decrease the costs associated with sorbent and disposal by about 30 percent over the base case studied in this report. Since these costs represent slightly less than 45 percent of the total annual cost, a potential savings of nearly 15 percent is possible.

This savings would be somewhat offset by increased capital costs associated with the higher flue gas temperatures. The net effect should amount to an approximate 10 percent reduction in the base cost of 2.60 mills per kWh. The new cost of 2.34 mills per kWh is lower than the limestone scrubbing cost of 4.08 mills per kWh by approximately 40 percent.

The use of MgO as a dry sorbent in a regeneration scheme was briefly examined. Kinetic data developed show that such a system, in conjunction with the baghouse FGD concept is not feasible.

2.13.4 Recommendations

The dry sorbent/baghouse flue gas desulfurization process appears to demonstrate an economic advantage over other currently available technologies for flue gas desulfurization, when applied to western power plants burning low sulfur coal as fuel. Thus, further demonstrations of the dry sorbent FGD process utilizing nahcolite as a sorbent should be pursued. Since the results of this analysis demonstrate that the dry sorbent process FGD system becomes economically advantageous when operated at temperatures in excess of those used for current demonstrations, a pilot plant study appears warranted to provide confirming technical and cost data for this study.

Since operation at extreme elevated temperatures of approximately 525°F (274°C) holds some additional promise for cost reduction due to increased utilization of the sorbent, the development of better test data at these temperatures should be pursued. The use of existing test facilities may be a possible route to obtain technical data in this area.

The data from tests currently in operation with Wheelabrator Frye, Inc., and Superior Oil Co., should be examined when they become available. Results from these tests should be used to confirm data obtained from other sources in developing the assumptions used in preparing this report. Additionally, these tests may provide some additional data on nahcolite utilization rates that can be expected at elevated temperatures.

2.14 TASK 24 PROCESS MEASUREMENT SYMPOSIUM

2.14.1 Objective

This task is devoted to the preparation and implementation of the Symposium on Process Measurements for Environmental Assessments. The conference was designed as a forum to present, discuss and evaluate measurement requirements, approaches and results within the broader context of the entire Environmental Assessment Program area. Considering the wide-ranging scope of the Environmental Assessment Program, a broad cross section of industry and government were invited to participate in the conference proceedings and discussions.

2.14.2 Discussion

The Process Measurement for Environmental Assessments Symposium was held at the Peachtree Plaza Hotel, Atlanta, Georgia, on February 13-15, 1978. The meeting proceeded with a minimum number of problem areas and, in general, has received high acclaim by the attendees. In general, the meeting speakers stayed within their allocated presentation period and minimal disruption was caused by coffee breaks and lunch time periods. A total of 163 attendees and participants took part in the proceedings.

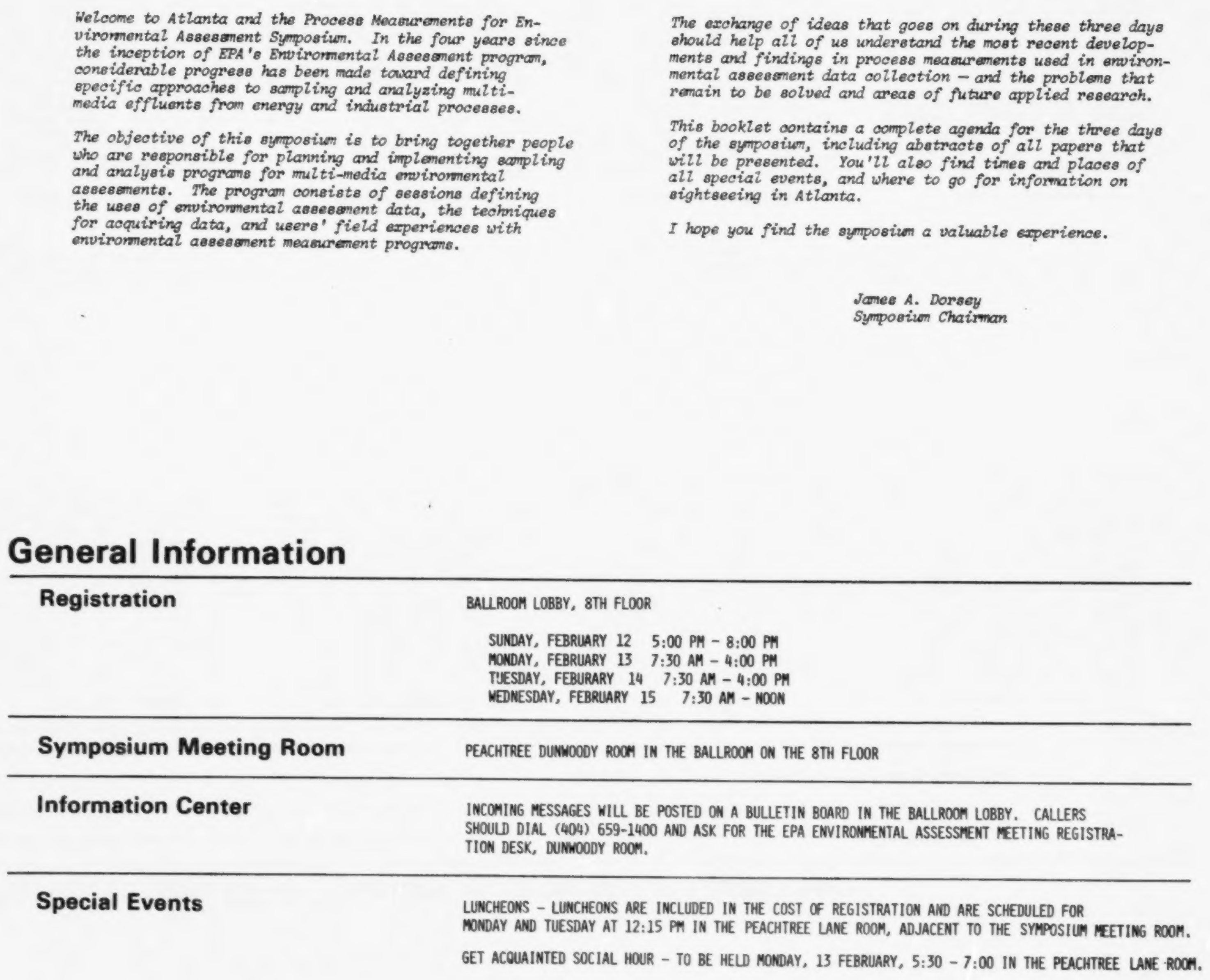
National coverage of the Symposium was afforded by the presence of Mr. Stanton S. Miller, Managing Editor of "Environmental Science and Technology". Special discussions were arranged with him and Dr. Gage, Dr. Statnick, Jim Dorsey, and John Burchard.

Mr. Miller, submitted a draft copy of the story highlighting the Environmental Assessment Symposium, which will be published in the May 1978 issue. The draft was reviewed and modified extensively to make it represent an accurate account of the technology transmitted in the Symposium. A similar draft was submitted to J. Dorsey, cognizant EPA Project Officer, for his review and editing. Stan Miller will now combine the two inputs and prepare a story for publication. Discussions with Mr. Miller will be held in Washington at OEMI to ensure that appropriate national recognition is obtained for future EPA-supported meetings of this type.

The major activity in completing final arrangements for the meeting was the preparation of the meeting program. Specifically, some of the speakers were tardy in presenting abstracts of their speeches and through a great deal of last-minute effort it was possible to put together the meeting program shown in Figure 24. The day after the program went to reproduction, the paper on Environmental Assessment of a Waste/Energy System from Midwest Research Institute was withdrawn because the sponsor of the project preferred to keep the information proprietary at this time. As a consequence of this cancellation, it was decided to reduce the meeting agenda by one paper and move the paper scheduled for Wednesday, 4:20 p.m. in the place of the originally scheduled 3:40 p.m. paper. An announcement to this effect was made by the Symposium Chairman during the initial announcement section of the meeting.

Other activities included the printing of special tickets for the two luncheons, social reception, tickets for a free drink (one to each attendee), and two types of badges (one for attendees and one for participants). In addition, a listing of recommended suggested restaurants in the Atlanta area, together with a map, was printed for use by the attendees at the meeting.

The Symposium Staff consisted of two members from EPA; Ms. Brenda Foil and Ms. Susan Sharpe, and three members from TRW; Ms. Mary McKay, Ms. Linda Schober and Mr. Chuck Weekley. The overall coordinator for the Symposium was Dr. Eugene Burns and the Symposium General Chairman was Mr. James Dorsey.



Welcome to Atlanta and the Process Measurements for Environmental Assessment Symposium. In the four years since the inception of EPA's Environmental Assessment program, considerable progress has been made toward defining specific approaches to sampling and analyzing multimedia effluents from energy and industrial processes.

The objective of this symposium is to bring together people who are responsible for planning and implementing sampling and analysis programs for multi-media environmental assessments. The program consists of sessions defining the uses of environmental assessment data, the techniques for acquiring data, and users' field experiences with environmental assessment measurement programs.

The exchange of ideas that goes on during these three days should help all of us understand the most recent developments and findings in process measurements used in environmental assessment data collection – and the problems that remain to be solved and areas of future applied research.

This booklet contains a complete agenda for the three days of the symposium, including abstracts of all papers that will be presented. You'll also find times and places of all special events, and where to go for information on sightseeing in Atlanta.

I hope you find the symposium a valuable experience.

James A. Dorsey
Symposium Chairman

General Information

Registration

BALLROOM LOBBY, 8TH FLOOR

SUNDAY, FEBRUARY 12 5:00 PM - 8:00 PM
MONDAY, FEBRUARY 13 7:30 AM - 4:00 PM
TUESDAY, FEBURARY 14 7:30 AM - 4:00 PM
WEDNESDAY, FEBRUARY 15 7:30 AM - NOON

Symposium Meeting Room

PEACHTREE DUNWOODY ROOM IN THE BALLROOM ON THE 8TH FLOOR

Information Center

INCOMING MESSAGES WILL BE POSTED ON A BULLETIN BOARD IN THE BALLROOM LOBBY. CALLERS SHOULD DIAL (404) 659-1400 AND ASK FOR THE EPA ENVIRONMENTAL ASSESSMENT MEETING REGISTRATION DESK, DUNWOODY ROOM.

Special Events

LUNCHEONS – LUNCHEONS ARE INCLUDED IN THE COST OF REGISTRATION AND ARE SCHEDULED FOR MONDAY AND TUESDAY AT 12:15 PM IN THE PEACHTREE LANE ROOM, ADJACENT TO THE SYMPOSIUM MEETING ROOM.

GET ACQUAINTED SOCIAL HOUR – TO BE HELD MONDAY, 13 FEBRUARY, 5:30 - 7:00 IN THE PEACHTREE LANE ROOM.

Figure 24. Symposium meeting program.

Participating EPA Officials and Session Chairmen

James A. Dorsey	**Symposium Chairman**
John K. Burchard	**Welcoming Address**
Stephen J. Gage	**Keynote Address**
Robert P. Hangebrauck	**Session Chairman**
Larry Johnson	**Session Chairman**
Charles H. Lochmuller	**Session Chairman**
Eugene A. Burns	**Session Chairman**
Karl J. Bombaugh	**Session Chairman**

Stephen J. Gage

is Acting Assistant Administrator for Research and Development for EPA. He is responsible for planning, directing and coordinating all Agency research activities covering air, water, toxic substances, radiation energy, pesticides and solid wastes. He joined EPA in 1974 as Acting Director of the Office of Energy Research; in 1975, he became the Deputy Administrator for Energy, Minerals and Industry. Prior to joining EPA, he was with the Council on Environmental Quality. During 1971-73, Dr. Gage was a White House Fellow. He joined the faculty at the University of Texas in 1965 and became Director of the Nuclear Reactor Laboratory in 1966. He received a B.S. in Mechanical Engineering from the University of Nebraska and M.S. and Ph.D. degrees from Purdue University.

Robert P. Hangebrauck

is the Director of the Energy Assessment and Control Division at the EPA's Industrial Environmental Research Laboratory. Mr. Hangebrauck received his B.S. from Cal-Tech in 1959. He has served with the EPA and its predecessor agencies for 17 years in various capacities, including Chief of the Clean Fuels and Energy Branch, Chief of the Demonstration Projects Branch, Control Systems Laboratory, and Assistant to the Director of the Bureau of Engineering and Physical Sciences. He is currently in charge of conducting the divisions' research and development programs to identify and control multimedia pollutants discharged in the environment from stationary sources.

Larry Johnson

is an Analytical Chemist in the Process Measurements Branch for EPA's Industrial Environmental Research Laboratory-RTP. He received his B.S. in Chemistry from Iowa State University and his Ph.D. in Chemistry from the University of Texas. Dr. Johnson manages contracts to develop screening procedures for environmental assessment programs and compound specific procedures for detailed analysis of complex samples from industrial processes. He is also responsible for evaluating the applicability of biological screening tests to complex effluent samples. He has specialized in the areas of organic sampling and analysis for trace components in industrial feed stocks and energy process effluents. Prior to joining EPA in 1972, Dr. Johnson was employed as an analytical chemist by PPG Industries and as a research chemist by Monsanto.

Eugene A. Burns

is Manager of the Chemistry and Chemical Engineering Program for Systems, Science and Software (S^3). He received his B.A. in Chemistry from Pomona College and his Ph.D. in Analytical Chemistry from Massachusetts Institute of Technology. Over the past 25 years, he has held a variety of research and management positions. Prior to joining S^3, Dr. Burns was employed by TRW for 15 years. As Manager, Chemistry Department, one of his responsibilities was energy-related environmental processes including the development of sampling and analysis methodology for characterizing process streams. Previous experience includes Chief of the Chemistry Section, Jet Propulsion Laboratory; and Head of the Analytical Chemistry Section, Stanford Research Institute's Propulsion Services Division.

John K. Burchard

is the Director of the Industrial Environmental Research Laboratory-RTP. He is responsible for the management of programs to develop and demonstrate cost-effective technologies to prevent, control, or abate pollution from industrial operations involving energy and mineral resources. He was recently appointed as senior ORD Official for EPA's Environmental Research Center in Research Triangle Park, N.C. Since joining EPA in 1970, he has served in several capacities — as Chief of the Laboratory's Technical Analysis Section, Chief of the Development Engineering Branch, and Assistant Director. Before joining EPA, Dr. Burchard worked in industry for 10 years. He holds B.S., M.S., and Ph.D. degrees in Chemical Engineering from Carnegie Tech.

James A. Dorsey

is Chief of the Process Measurements Branch in the EPA's Industrial Environmental Research Laboratory-RTP. He received his B.S. in Chemistry from Florida State University. He is responsible for integrated in-house/contract programs for the development and application of measurement procedures for energy and industrial processes. Prior to joining EPA in 1964, Jim was employed by Shell Oil Company as a research chemist. He has over 20 years of experience developing sampling and analysis techniques using advanced methods of instrumental analysis. Current studies include the sampling and analysis of organic and inorganic trace materials in gas, liquid and solid feed, product and waste streams. Jim is a member of the American Chemical Society and the Air Pollution Control Association.

Charles H. Lochmuller

is an Associate Professor of Chemistry with Duke University. He is a consultant to the EPA Industrial Environmental Research Laboratory/RTP Process Measurement Branch in the areas related to the development of analytical methodology for environmental assessment and a member of its advisory panel on organic analysis. Prof. Lochmuller was one of the originators of the staged sampling and analysis protocol for environmental assessment process measurements. He received his B.S. in Chemistry from Manhattan College and his M.S. and Ph.D. degrees in Analytical Chemistry from Fordam University. His research interests are in the area of fundamental aspects of the molecular basis for selectivity in chemical separation methods. His recent work includes areas of charged particle induced x-ray emission analysis and Fourier Transform Magnetic Resonance Spectroscopy.

Karl J. Bombaugh

is a Principal Scientist at Radian Corporation where he is responsible for the development of strategies and systems for environmental tests. He obtained his B.S. in Chemistry from Juniata College. Over the past thirty years, he has held a variety of positions in both research and management. His experience covers a broad range of analytical and process technology, including infrared spectrometry, both gas and liquid chromatography, and on-stream analysis. As Vice-president for Research and Development at Waters Associates, he directed a group who pioneered in the development of modern high pressure liquid chromatography. He has authored more than fifty publications including chapters in several books. He has served on the editorial advisory board of the Journal of Chromatographic Science, and the Chemical Rubber Handbook of Chromatography. He is now Chairman Emeritus of

Figure 24. (Continued)

NOTE: Approximately 10 minutes have been reserved in the 40-minute presentations to accommodate questions and answers. Speakers names appear in italics.

Monday, February 13

8:40 a.m. WELCOMING REMARKS

John K. Burchard, Director, IERL-RTP, EPA

8:50 a.m. KEYNOTE ADDRESS

PROCESS MEASUREMENTS FOR ENVIRONMENTAL ASSESSMENT

Stephen J. Gage, Acting Assistant Administrator for Research and Development, EPA

9:20 a.m. ANNOUNCEMENTS

James A. Dorsey, Symposium Chairman, Chief, Process Measurements Branch, IERL-RTP, EPA

9:25 a.m.

Environmental Assessment Overview, Session I

R. P. Hangebrauck, Director, Energy Assessment and Control Division, IERL-RTP, EPA, Session Chairman

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9:30 a.m.

OEMI OVERVIEW OF ENVIRONMENTAL ASSESSMENT

Robert M. Statnick and Dave Berg, Office of Energy, Minerals and Industry, EPA

The environmental assessment program which has been ongoing for about four years is to develop an EPA data base which can be utilized to set standards for air emissions, water effluents, and solid waste disposal practices. This program has several major components; they are evaluation of emission rates, evaluation of the degree of control which is achieved with conventional effluent/emission control equipment, evaluation of the biological activity of environmental samples, and estimation of "safe" emission rates. The program which will be discussed during these proceedings will focus upon the techniques which will be utilized to acquire these environmental samples and to analyze them. This paper will present an overview of the data requirements specified in recent legislation to which the environmental assessment program data base can input.

10:10 a.m. **Coffee Break**

10:40 a.m.

THE DOE INTEGRATED ASSESSMENT PROGRAMS

Ray Cooper, Division of Regional Assessments, E&S, DOE

The Integrated Environmental Assessment programs of DOE are designed to support the Assistant Secretary for the Environment in the conduct of his responsibilities.

In order to fulfill these responsibilities, particularly those associated with policy guidance for the Department, there are three kinds of assessment activities which must be carried out. Since the Department is responsible for developing a national energy policy, national environmental assessments of this policy are required. Technology assessments must be done in order to explore environmental issues which affect technology development decisions and the levels of environmental control required. Finally, regional environmental assessments must be carried out because environmental and social impacts of energy policies and technological developments are very dependent upon the specific characteristics of the region involved.

Examples of all three types of assessment were recently completed in connection with the National Energy Plan as submitted to Congress. A national assessment of the environmental impacts associated with the plan was made using a comprehensive simulation model based on the SEAS system calibrated to the NEP assumptions for the period 1975 to 2000. Regional assessments were made of the impact of the plan on New England and on Region VI where conversion from oil and gas to coal is expected. Finally, technology assessments were made of the prospects for solar energy and of the impacts of the coal part of NEP on water needs, water quality, solid waste, and local socioeconomic well-being.

11:20 a.m.

RELATED EPRI PROGRAMS

Ralph Perhac, Electric Power Research Institute

Present emphasis in EPRI's Environmental Assessment Department is on atmospheric pollution arising from coal-burning power plants. The main goal of the Department is to assess the impact of the nation's increasing energy production on biota, particularly on people. The identification of pollutants, their physico-chemical nature, and their fate is the charge of the Department's Physical Factors Program. New measuring procedures have been developed or improved; including matrix isolation spectroscopy for PAH analysis, and lidar for remote measurement of atmospheric pollutants. Future research direction in pollutant identification and characterization will be on techniques for defining chemical speciation and on identification of new classes of pollutants, especially those related to coal conversion processes. A number of field studies have been undertaken aimed at gathering data for elucidating reaction mechanisms and fate of pollutants. The $7 million SURE program is a massive effort in measuring air quality in the Northeast in an effort to clarify the relation between regional, ambient concentrations of secondary pollutants and emissions of primary precursors.

Figure 24. (Continued)

12:15 p.m. **Luncheon — Peachtree Lane Room**

1:30 p.m. Environmental Assessment Overview, Session II

James Dorsey, Chief, Process Measurement Branch, IERL-RTP, EPA, Session Chairman

1:30 p.m.

EPA AIR PROGRAMS' USE OF ENVIRONMENTAL ASSESSMENTS

Richard G. Rhoads, Director, Control Programs Development Division, OAQPS, EPA

Under the Environmental Protection Agency's legislative authority, a variety of strategies are available for controlling air pollution. Principal among these are direct emission standards for specific new sources which represent the best demonstrated control technology, direct emission standards for both new and existing sources to minimize specific hazardous pollutants, ambient air quality standards for selected pollutants which are necessary to protect the public health and welfare, mobile source emission controls and fuel additive standards which assist in protecting the public health and welfare, and programs to prevent significant deterioration of air quality.

This presentation describes these various alternative strategies, and discusses how environmental assessments can assist in (1) setting priorities for the pollutants and sources to be controlled, (2) selecting the strategy or combination of strategies to be employed, and (3) assessing the necessary or desired level of control.

2:10 p.m.

AN INTEGRATED APPROACH TO THE ASSESSMENT AND CONTROL OF INDUSTRIAL POLLUTION PROBLEMS

Eugene E. Berkau, Director, Industrial Pollution Control Division, IERL-Ci, EPA

EPA now has comprehensive legislative and court mandates for regulating all pollution resulting from the production and use of industrial chemicals and products. Emphasis is being placed on toxic and hazardous pollutants. To aid EPA in focusing its attention and future efforts on those pollution problems which have the greatest health and ecological impacts, EPA has developed in one organizational unit an approach for assessing simultaneously the environmental impacts of industrial pollution discharged to the air, water, land and municipal systems. This multimedia approach necessarily involves the active participation of the appropriate EPA regulatory components and industry. Field sampling and RD&D programs are initiated based upon the outcome of the integrated industrial assessment approach.

2:50 p.m.

SOURCE ASSESSMENT METHODOLOGY

Thomas W. Hughes, Monsanto Research Corp.

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for ensuring that pollution control technology is available for stationary sources to meet the goals of environmental legislation. If control technology is unavailable, inadequate, uneconomical or socially unacceptable, then financial support is provided for the development of the needed control techniques for industrial and extractive processes.

IERL performs source assessments for determining the need to reduce emissions and discharges from pollution sources. Health effects data, environmental dispersion models, monitoring data and engineering information are used in performing the source assessment. IERL decisions based on source assessments are subject to errors because of the inherent uncertainties in the data used to generate decision-making information. This paper presents a discussion of the steps involved in performing source assessments, information used as an aid in IERL decision making, elements of uncertainty in IERL decision making, and specific guidelines to be used in performing source assessments to minimize incorrect IERL decisions.

3:30 p.m. **Coffee Break**

3:45 p.m.

RELATED HEALTH EFFECTS PROGRAMS

Shahbeg Sandhu, HERL-RTP, EPA

The growing concern for human health safety due to the ever increasing presence of a wide variety of chemicals in our environment has been amplified by studies showing strong associations between chemical, carcinogenesis, and mutagenesis.

The diversity of genotoxic insults inflicted by environmental chemicals and the need to test a large number of chemicals, necessitates the use of multi-level approach employing a battery of tests at each level.

The emphasis on Level 1 battery is on the detection of gene mutation and primary DNA damage. Included in the battery are bioassays using bacterial species; lower eukaryotic species and tests for cytotoxicity.

The purpose of the Level 2 battery is to confirm or refute the results obtained in Level 1. Included in Level 2 are specific assays using mammalian cells in culture for point mutations, chromosomal aberrations and neoplastic transformation.

The results obtained utilizing Level 1 bioassays for the analysis of parent compounds, metabolites, and complex mixtures will be discussed.

Figure 24. (Continued)

4:25 p.m.

BIOLOGICAL TESTING METHODOLOGY

Kenneth M. Duke, Battelle Columbus Laboratories

Biological procedures for testing feedstocks and waste streams of individual processes have been developed as part of EPA's phased approach to Environmental Source Assessment. The objectives of the first phase or level of biological testing are to (1) provide preliminary data on the biological effects of feedstocks and waste streams, (2) identify problems in implementing the tests on the streams, and (3) prioritize the streams according to their relative hazard. The Bioassay Subcommittee of IERL-RTP's Environmental Assessment Steering Committee has developed a Level 1 biological test protocol to meet these objectives. The protocol includes four health tests and eight ecological tests to be implemented on liquid, solid, and gaseous streams. Pilot studies are underway to test and refine this protocol. Results indicate the phased approach is effective in directing environmental assessment activities.

5:05 p.m. **Adjourn**

5:30 p.m. — 7:00 p.m. **Social Reception — Peachtree Lane Room**

Tuesday, February 14

8:30 a.m.

Measurement Technologies, Session I

Larry Johnson, IERL-RTP, EPA, Session Chairman

8:30 a.m.

SOURCE ASSESSMENT SAMPLING SYSTEM DESIGN AND DEVELOPMENT

David Blake and J. M. Kennedy, Acurex/Aerotherm

The Source Assessment Sampling System (SASS) is the primary sampling tool for Level 1 gaseous and particulate emissions. The design philosophy of the SASS is reviewed, including an analysis of alternate configurations that were considered during the conceptual design phase. Accuracy limitations of the SASS for particulate collection stems primarily from difficulties in accurately calibrating the cyclones. Cyclone calibration methods and recent results are discussed. Possible SASS modifications to increase utility and accuracy are also presented.

9:10 a.m.

FIELD EVALUATION OF THE SASS TRAIN AND LEVEL 1 PROCEDURES

Franklin Smith, Eva D. Estes and Denny E. Wagoner, Research Triangle Institute

The results of a two-phased evaluation of Level 1 environmental assessment procedures are presented. Phase one was a field evaluation of the SASS train. Three sample runs were made with two SASS trains sampling simultaneously and from approximately the same sampling point. A method-5 train was used to estimate the "true" particulate loading. Comparisons of the SASS trains are made for total particulate, particle size distribution, organic classes, and trace elements. Phase two consisted of providing three participating organizations with control samples to challenge the spectrum of Level 1 analytical procedures. Estimates of intra- and inter-laboratory precision are made.

9:50 a.m.

INORGANIC EMISSIONS MEASUREMENTS

Ray F. Maddalone and Lorraine E. Ryan Applied Technology Division, TRW DSSG

The analysis of inorganic compounds requires the coordinated use of a variety of analytical techniques. This paper describes an inorganic analysis scheme consisting of an initial sample characterization (stability, elemental composition, and morphology), bulk composition characterization (anion composition, surface characterization, and x-ray diffraction data) and individual particle characterization (single particle elemental composition, x-ray diffraction pattern, and morphology). The use of Multimedia Environmental Goal (MEG) compounds and their Minimum Acute Toxicity Effluent (MATE) values to focus analysis activities will be described. Data from a recent field test using this approach will be used to illustrate the information derived from these methods.

10:30 a.m. **Coffee Break**

10:45 a.m.

MEASUREMENT OF ORGANIC EMISSIONS FOR ENVIRONMENTAL ASSESSMENT

Philip L. Levins, Arthur D. Little, Inc.

Systematic measurement methods are being developed for the determination of organic species in emission and process streams. The methods are structured on the Phased approach developed by the Process Measurements Branch of IERL-RTP. Level 1 analysis methods have been tested and a reporting format developed which is consistent with a variety of assessment objectives. Level 2 procedures are focused on general broad spectrum analysis protocols and specific analyte procedures such as for PCB's, PAH, etc. Macreticular resins are being studied quantitatively to develop improved air and water sampling methods.

11:25 a.m.

A CRITIQUE OF ORGANIC LEVEL 1 ANALYSIS

Peter W. Jones and Robert J. Jakobsen Battelle Columbus Laboratories

An objective review of organic Level 1 analysis is provided. Present strengths and weaknesses are pointed out and recommendations are made concerning how improvements may be made. Areas which are addressed include the adequacy of sample size, the optimum LC separation scheme – possible use of HPLC, problems associated with contamination – both in the field and as a result of adsorbent degradation, the utility of FTIR, and LRMS analysis.

Figure 24. (Continued)

12:15 p.m. **Luncheon — Peachtree Lane Room**

1:30 p.m.

Measurement Technologies, Session II

Charles Lochmuller, Duke University, Session Chairman

1:30 p.m.

FUGITIVE EMISSIONS MEASUREMENT TECHNIQUES FOR ENVIRONMENTAL ASSESSMENTS

Henry J. Kolnsberg, The Research Corporation of New England

The sampling and measurement techniques currently being employed or developed to determine the impact of industrial fugitive emissions on the environment are described. Three general sampling techniques for airborne fugitive emissions and one for waterborne fugitive emissions as stormwater runoff are presented and evaluated with respect to their inherent accuracies and limitations. Site-specific modifications of the general techniques used in recent studies at a variety of industrial locations are described and the results of the measurement programs reviewed. Efforts toward the development of a fugitive ambient sampling train for the measurement of airborne particulate and organic emissions are summarized.

2:10 p.m.

SAMPLING AND ANALYSIS PROCEDURES FOR SCREENING OF INDUSTRIAL EFFLUENTS FOR PRIORITY POLLUTANTS

William A. Telliard, Chief, Energy and Mining Branch, Effluents Guidelines Division, OWPS, EPA

The Environmental Protection Agency agreed to review and revise regulations based on the Best Available Technology Economically Achievable for effluents in 21 industries categories, as a settlement of several cases in the District Court for the District of Columbia.

An integral part of this process is a technical study to determine whether or not compounds from a list of 65 materials (single compounds and undefined classes of compounds) exist in industrial waste waters. The Effluent Guidelines Division in EPA has established an unambiguous list of 129 compounds, referred to as priority pollutants, which it believes fulfills the requirements of the court order and can be determined analytically.

To maintain consistent sampling and analytical procedures for 21 industrial studies, EPA has developed a protocol of the sampling and analytical methods to be used for the screening of priority pollutants in waste water. This protocol represents the incorporation of the current state of the art procedures for the sampling and analysis of the priority pollutants. These analytical procedures include: purge and trap – gas chromatography – mass spectrometry (GC/MS) for volatile organic compounds; semi-volatile organics are done by a liquid-liquid extraction with GC/MS and metals are determined using an inductively coupled argon plasma emission spectrometer.

2:50 p.m.

ALTERNATIVE LEVEL 1 ANALYSIS METHODS

Karl Bombaugh, Radian Corporation

This presentation provides a description of some modifications and additions to the Level 1 analysis scheme that were used to characterize the emissions from coal gasification plants. While some of these modifications go beyond the intent of the Level 1 analyses, the experience gained from their use should be of value to others performing environmental analyses.

3:30 p.m. **Coffee Break**

3:45 p.m.

SYNTHETIC FUELS PRODUCTION: ANALYSIS OF PROCESS BY-PRODUCTS FROM A LABORATORY SCALE COAL GASIFIER

Charles M. Sparacino, Research Triangle Institute

Methodology has been developed for the analysis of the volatile (gas stream components) and non-volatile (tars and condensates) materials produced as by-products during the gasification of coal. Volatile materials are collected by entrapment on polymeric sorbents, and analyzed directly by GC/MS. Non-volatile materials are solvent extracted and/or partitioned, and the resulting fractions are analyzed by GC/MS. Qualitative analyses for each sample type have been carried out; quantitative approaches are under development.

4:25 p.m.

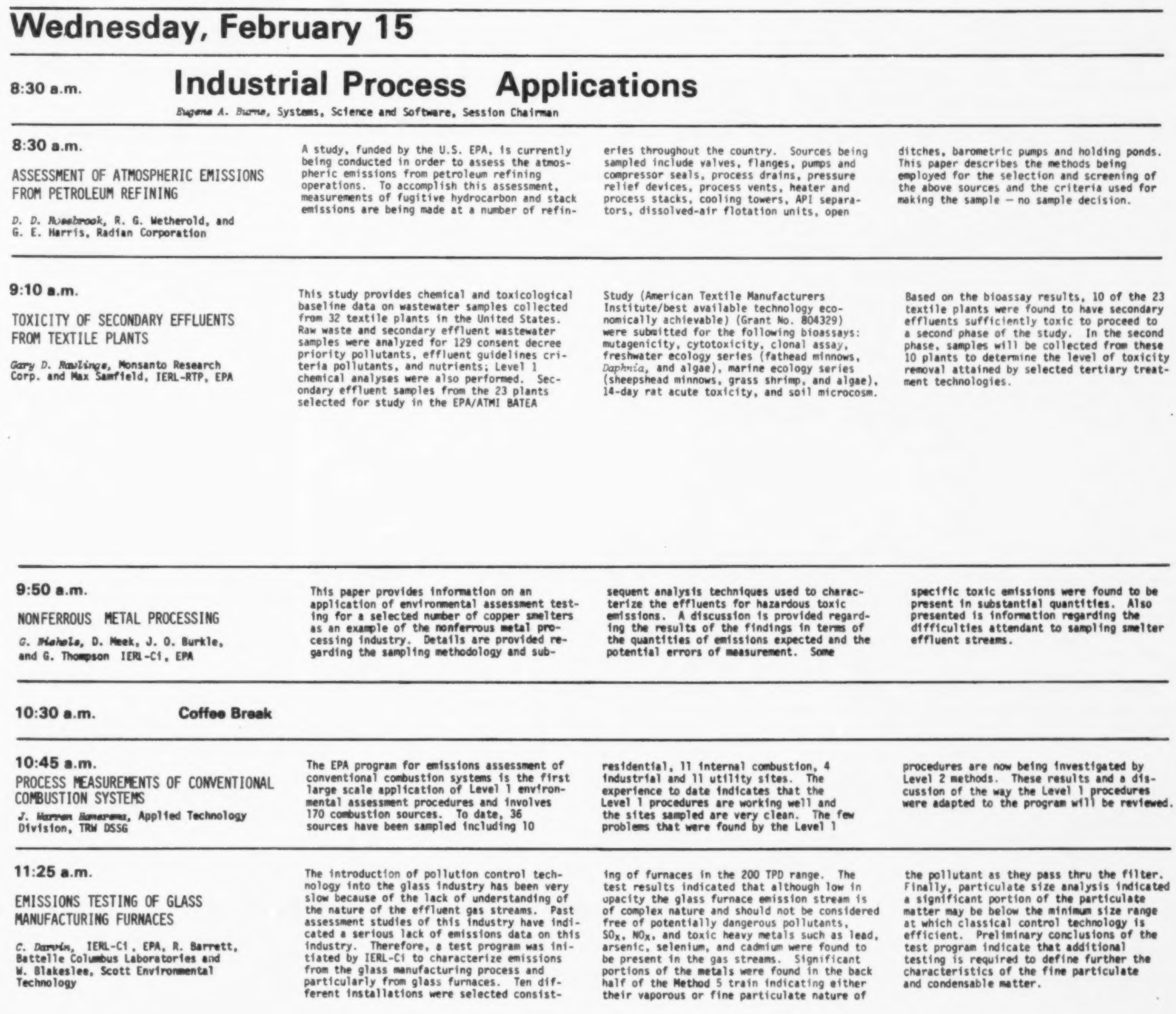
VAPOR-TO-PARTICLE CONVERSION OF ORGANIC SPECIES FOLLOWING FOSSIL FUEL COMBUSTION

D. F. S. Natusch, M. Schure, and B. A. Tomkins, Colorado State University

A mechanism of vapor-to-particle conversion of organic species by adsorption onto particulate material is presented. Theoretical consideration of this process predicts that polycyclic aromatic and long chain aliphatic species can undergo essentially quantitative adsorption at temperatures encountered directly following emission to the atmosphere; that the process can occur in the order of seconds; and that the process is complete within a short distance of the emission source. The results of both laboratory and field experiments strongly support these predictions and indicate that adsorption is of primary importance in vapor-to-particle conversion. The significance of this finding with respect to the design and conduct of sampling procedures is discussed.

5:05 p.m. **Adjourn**

Figure 24. (Continued)



Wednesday, February 15

8:30 a.m. **Industrial Process Applications**

Eugene A. Burns, Systems, Science and Software, Session Chairman

8:30 a.m.

ASSESSMENT OF ATMOSPHERIC EMISSIONS FROM PETROLEUM REFINING

D. D. Rosebrook, R. G. Wetherold, and G. E. Harris, Radian Corporation

A study, funded by the U.S. EPA, is currently being conducted in order to assess the atmospheric emissions from petroleum refining operations. To accomplish this assessment, measurements of fugitive hydrocarbon and stack emissions are being made at a number of refineries throughout the country. Sources being sampled include valves, flanges, pumps and compressor seals, process drains, pressure relief devices, process vents, heater and process stacks, cooling towers, API separators, dissolved-air flotation units, open ditches, barometric pumps and holding ponds. This paper describes the methods being employed for the selection and screening of the above sources and the criteria used for making the sample — no sample decision.

9:10 a.m.

TOXICITY OF SECONDARY EFFLUENTS FROM TEXTILE PLANTS

Gary D. Rawlings, Monsanto Research Corp. and Max Samfield, IERL-RTP, EPA

This study provides chemical and toxicological baseline data on wastewater samples collected from 32 textile plants in the United States. Raw waste and secondary effluent wastewater samples were analyzed for 129 consent decree priority pollutants, effluent guidelines criteria pollutants, and nutrients; Level 1 chemical analyses were also performed. Secondary effluent samples from the 23 plants selected for study in the EPA/ATMI BATEA Study (American Textile Manufacturers Institute/best available technology economically achievable) (Grant No. 804329) were submitted for the following bioassays: mutagenicity, cytotoxicity, clonal assay, freshwater ecology series (fathead minnows, *Daphnia*, and algae), marine ecology series (sheepshead minnows, grass shrimp, and algae), 14-day rat acute toxicity, and soil microcosm. Based on the bioassay results, 10 of the 23 textile plants were found to have secondary effluents sufficiently toxic to proceed to a second phase of the study. In the second phase, samples will be collected from these 10 plants to determine the level of toxicity removal attained by selected tertiary treatment technologies.

9:50 a.m.

NONFERROUS METAL PROCESSING

G. Nichols, D. Meek, J. O. Burkle, and G. Thompson IERL-Ci, EPA

This paper provides information on an application of environmental assessment testing for a selected number of copper smelters as an example of the nonferrous metal processing industry. Details are provided regarding the sampling methodology and subsequent analysis techniques used to characterize the effluents for hazardous toxic emissions. A discussion is provided regarding the results of the findings in terms of the quantities of emissions expected and the potential errors of measurement. Some specific toxic emissions were found to be present in substantial quantities. Also presented is information regarding the difficulties attendant to sampling smelter effluent streams.

10:30 a.m. **Coffee Break**

10:45 a.m.

PROCESS MEASUREMENTS OF CONVENTIONAL COMBUSTION SYSTEMS

J. Warren Hamersma, Applied Technology Division, TRW DSSG

The EPA program for emissions assessment of conventional combustion systems is the first large scale application of Level 1 environmental assessment procedures and involves 170 combustion sources. To date, 36 sources have been sampled including 10 residential, 11 internal combustion, 4 industrial and 11 utility sites. The experience to date indicates that the Level 1 procedures are working well and the sites sampled are very clean. The few problems that were found by the Level 1 procedures are now being investigated by Level 2 methods. These results and a discussion of the way the Level 1 procedures were adapted to the program will be reviewed.

11:25 a.m.

EMISSIONS TESTING OF GLASS MANUFACTURING FURNACES

C. Darvin, IERL-Ci, EPA, R. Barrett, Battelle Columbus Laboratories and W. Blakeslee, Scott Environmental Technology

The introduction of pollution control technology into the glass industry has been very slow because of the lack of understanding of the nature of the effluent gas streams. Past assessment studies of this industry have indicated a serious lack of emissions data on this industry. Therefore, a test program was initiated by IERL-Ci to characterize emissions from the glass manufacturing process and particularly from glass furnaces. Ten different installations were selected consisting of furnaces in the 200 TPD range. The test results indicated that although low in opacity the glass furnace emission stream is of complex nature and should not be considered free of potentially dangerous pollutants, SO_x, NO_x, and toxic heavy metals such as lead, arsenic, selenium, and cadmium were found to be present in the gas streams. Significant portions of the metals were found in the back half of the Method 5 train indicating either their vaporous or fine particulate nature of the pollutant as they pass thru the filter. Finally, particulate size analysis indicated a significant portion of the particulate matter may be below the minimum size range at which classical control technology is efficient. Preliminary conclusions of the test program indicate that additional testing is required to define further the characteristics of the fine particulate and condensable matter.

Figure 24. (Continued).

12:05 p.m. **Lunch Break**

1:30 p.m.

Energy Process Applications

Karl Bombaugh, Radian Corporation, Session Chairman

1:30 p.m.

COMPREHENSIVE ANALYSIS OF EMISSIONS FROM FLUIDIZED-BED COMBUSTION PROCESSES

K. S. Murthy, J. E. Howes, and H. Nack, Battelle Columbus Laboratories and R. D. Hoke, Exxon Research and Engineering Co.

Results of the comprehensive analysis of emissions from a pressurized fluidized-bed combustion unit (the Exxon Miniplant) will be described as an illustration of the methodology. The results will be discussed in the context of the overall environmental assessment of the process being conducted by the United States Environmental Protection Agency. The comprehensive analysis of the fluidized-bed combustion emissions and process streams involved approximately 740 measurements on about 90 samples using more than 40 different inorganic, organic, and physical analytical methods. A discussion will be presented covering the methodology which was used for sample preparation, inorganic analysis, organic analysis, and physical measurements. Also, results of the analyses will be presented with the emphasis on quality control procedures and accuracy and precision estimates derived from the data.

2:10 p.m.

ENVIRONMENTAL ASSESSMENT PROGRAM FOR THE HYGAS PROCESS

L. J. Anastasia, W. G. Bair, and D. P. Olson, Illinois Institute of Gas Technology

The Institute of Gas Technology is developing an environmental assessment of the HYGAS process under contract to the U.S. Department of Energy (DOE). HYGAS is a second-generation coal gasification process which uses hydrogen in a fluidized bed at high pressure and temperature to maximize production of methane (SNG) from all types of coal. HYGAS process development is carried out in a 3 ton/hr pilot plant which produces a nominal 1.5MM SCFD of pipeline-quality gas at 1000 Btu/ft^3.

The main objective of the HYGAS Environmental Assessment Program is to obtain and interpret experimental data from the pilot plant systematically to estimate pollutant production for demonstration and commercial-scale HYGAS coal gasification plants. Priorities have been established to operate systems for sampling, analysis, and data evaluation to define the fate of potential pollutants generated during operation of the pilot plant. The assessment methodology for environmental data acquisition and interpretation features these sequential objectives:

- Identification of potential pollutants in plant effluent streams,
- Development of sampling, preservation, and analytical techniques,
- Process unit, stream, and species selection, and
- Quantitative descriptions of significant pollutants.

2:50 p.m.

CHARACTERIZATION OF SYNTHOIL/ SYNTHANE PROCESSES

A. G. Sharkey, Jr., Pittsburgh Energy Research Center

Much of the analytical data required for process development is also useful in developing control technology and can assist in environmental assessments. As part of the coal gasification and liquefaction process development programs at the Pittsburgh Energy Research Center, extensive determinations have been made of the organic and trace element components in process streams. An overview will be presented of the major features of the process streams, using the SYNTHANE and SYNTHOIL processes as examples. Recently completed trace element balances and investigations of the heterocyclic nitrogen and sulfur compounds associated with coal liquefaction products will be described. Examples of the use of a high-resolution mass spectrometry procedure to screen for possible hazardous compounds will be given. Possible revisions in proposed models for the structure of coal will be reviewed in the light of new spectral data. Limitations to the applications of conventional petroleum analytical methods to coal-derived fuels will be discussed and required separation procedures described. Several of the remaining challenges for the analysis of synfuels will be reviewed.

3:30 p.m. **Coffee Break**

3:45 p.m.

ASSESSMENT OF A PROTOTYPE WASTE/ ENERGY SYSTEM

M. F. Marcus, H. H. Miller and P. H. Cramer, Midwest Research Institute

The initial process assessment of a prototype energy system indicated a possible water effluent environmental problem. Therefore, intensive sampling and analysis was performed. The results from the organic characterization included the following analysis: EPA Level 1; EPA Priority Pollutants; polynuclear aromatic hydrocarbons; and polychlorinated biphenyls. The effectiveness of an aerobic wastewater treatment system was also evaluated by characterization of organic compounds before and after treatment. The EPA Level 1 results are from methods that include: gas chromatography (GC); infrared; liquid chromatography; and direct inlet low resolution mass spectrometry. The EPA Priority Pollutant results are on sample fractions which include: volatiles, acid extractables; base-neutral extractables; and pesticides. The principal analysis technique is GC/MS on packed columns with capillary GC/MS on selected samples. The GC/MS data were also interpreted for nonpriority pollutants for a further characterization of the organic compounds. The sample preparation and analysis by GC/MS were optimized for polynuclear aromatic hydrocarbons (PNA). Selected samples were further analyzed by high resolution MS to characterize further the PNA present in the samples. Polychlorinated biphenyl (PCB) analysis consisted of: sample cleanup to isolate PCB– containing fraction, derivatization of this fraction to convert any PCB to decachlorobiphenyl and detection by GC with electron capture. Those sample fractions for which PCB was detected are analyzed by GC/MS of the underivatized sample fraction to confirm identification.

4:25 p.m.

ENVIRONMENTAL MEASUREMENT PROGRAM AT THE PARAHO SHALE OIL RECOVERY FACILITY

Jack E. Cotter, Environmental Engineering Division, TRW

A multi-media sampling and analysis program was conducted in 1976 and 1977 at Paraho's shale oil demonstration plant in Colorado. The work was sponsored by IERL-Cincinnati. A number of different sampling methodologies and analytical procedures were used, with the objective of comparing measurement techniques for accuracy, practicality, and cost of implementation. A brief discussion of the Paraho process is included, and the sampling and analysis rationale is given. Qualitative and quantitative findings are reported. Particular attention is given to the special needs of environmental assessment of vapor, liquid, and solid waste by-products from oil shale operations.

5:05 p.m. **Adjourn**

Figure 24. (Continued)

Symposium At A Glance

MONDAY, FEBRUARY 13TH

8:40	Welcoming Remarks	J. Burchard, IERL-RTP, EPA
8:50	Keynote Address	S. J. Gage, AA ORD, EPA
9:20	Announcements	J. Dorsey, IERL-RTP, EPA

ENVIRONMENTAL ASSESSMENT I, R. Hangebrauck, IERL-RTP, EPA

9:30	OEMI Overview	R. Statnick, OEMI, EPA
10:10	Coffee Break	
10:40	DOE Integrated Assessment	R. Cooper, E&S, DOE
11:20	EPRI Programs	R. Perhac, EPRI
12:15	Luncheon, Peachtree Lane Room	

ENVIRONMENTAL ASSESSMENT II, J. Dorsey, IERL-RTP, EPA

1:30	OAQPS Use of EA	R. Rhoads, OAQPS, EPA
2:10	Industrial Process EA	E. Berkau, IERL-Ci, EPA
2:50	Source Assessment Methods	T. Hughes, Monsanto
3:30	Coffee Break	
3:45	Health Effects Programs	S. Sandhu, HERL, EPA
4:25	Level 1 Bioassay Methods	K. Duke, Battelle
5:30 - 7:00	Social Reception, Peachtree Lane Room	

TUESDAY, FEBRUARY 14TH

MEASUREMENT TECHNOLOGIES I, L. Johnson, IERL-RTP, EPA

8:30	SASS Train Development	D. Blake, Aerotherm
9:10	Field Evaluation of SASS and Level 1	F. Smith, RTI
9:50	Inorganic Emissions	R. Maddalone, ATD, TRW
10:30	Coffee Break	
10:45	Organic Emissions	P. Levins, ADL
11:25	Level 1 Critique	P. Jones, Battelle
12:15	Luncheon, Peachtree Lane Room	

MEASUREMENT TECHNOLOGIES II, C. Lochmuller, Duke U.

1:30	Fugitive Emissions	H. Kolnsberg, TRC
2:10	Priority Pollutants Analysis	W. Telliard, EGD, EPA
2:50	Alternative Level 1	K. Bombaugh, Radian
3:30	Coffee Break	
3:45	Coal Tar Analysis	C. Sparacino, RTI
4:25	POM Characterization	D. Natusch, Col. St. U.
5:05	Adjourn	

WEDNESDAY, FEBRUARY 15TH

INDUSTRIAL PROCESSES, E. Burns, S^3

8:30	Petroleum Refining	D. Rosebrook, Radian
9:10	Textile Industries	G. Rawlings, Monsanto
9:50	Non-Ferrous Metals	G. Nichols, IERL-Ci, EPA
10:30	Coffee Break	
10:45	Conventional Combustion Systems	W. Hamersma, ATD, TRW
11:25	Glass	C. Darvin, IERL-Ci, EPA
12:00	Lunch Break	

ENERGY PROCESSES, K. Bombaugh, Radian

1:30	FBC Processes	K. Murthy, Battelle
2:10	Hygas	L. Anastasia, IIGT
2:50	Synthoil/Synthane	J. Sharkey, PERC, DOE
3:30	Coffee Break	
3:45	Waste/Energy System	M. Marcus, MRI
4:25	Oil Shale Processes	J. Cotter, EED, TRW
5:05	Adjourn	

Figure 24. (Continued)

2.15 TASK 26 TOTAL PARTICULATE MASS EMISSION SAMPLING ERRORS

2.15.1 Objective

The task objective was to obtain an estimate of sampling errors in the measurement of total particulate mass emissions from stationary sources. More specifically, it was desired to determine the accuracy of particulate mass emissions as determined by techniques in "IERL-RTP Procedures Manual: Level 1 Environmental Assessment."

2.15.2 Approach

The approach taken was to perform a standard error analysis, based on the relevant equation of motion, hardware characteristics of sampling systems, and sampling methodology. The result of the effort was a fifty-page report which concluded that the accuracy of the SASS train as used for Level 1 assessment work has an accuracy of "factor of ± 2 to 3" or better, as required by the Level 1 procedures.

The draft final report was submitted at the completion of 100 technical hours. At the request of the Project Officer, there was an extensive rewrite, including putting most of the technical derivations in appendices, in order to obtain an optimum format for the designated audience.

2.15.3 Technical Discussion

The error analysis was quite straightforward. The basic approach used was a fully entrained particle model with a factor to allow for gas/particle slip. Given this equation of motion, a standard error analysis as was done in EPA-600/2-76-203, "Flow and Gas Sampling Manual." The error equations were derived, and individual error terms were evaluated using instrument characteristics, typical source characteristics, and methodology details.

Basic results showed a SASS train accuracy of about a factor of ± 2 or better at places such as stacks and inlets to control devices, and a factor of ± 3 at a control device outlet. These accuracies are for a single point sample. Results also showed that the SASS train accuracy can be dramatically improved, to about ± 25 percent or better, by using a sixteen point traverse in lieu of a single sample point. Along with the SASS train evaluation, calculations were also performed for a "maximum accuracy" train — a hypothetical sampling train using the best available commercial hardware. Since for single point sampling the greatest error is due to particle stratification in the stream, the single point accuracy of the SASS and "maximum accuracy" train was found to be virtually identical. For a 16-point traverse, however, the calculated accuracy of the "maximum accuracy" train was in the range of 10% - 16%, significantly better than the SASS train. The most important result as far as IERL is concerned was that the accuracy of the SASS train and Method 1 procedures was found to be as claimed.

2.15.4 Summary and Recommendations

From this task it was found:

1) Level 1 total particulate mass emission assessments:
   - A SASS train operated in accordance with "IERL-RTP Procedures Manual, Level 1 Environmental Assessment" sampling at a single point will have a sampling accuracy of a factor of ±2 or better in most locations such as stacks or control device inlets. Under worst case conditions, such as at an ESP outlet, it will have an accuracy of about a factor of ±3.
   - The degree of anisokinetic sampling induced by the SASS train design and operation has a negligible effect on system accuracy.
   - In single point sampling, the mapping error (non-representativeness of the selected point) will be the largest individual error in the system.
   - Sampling accuracy using the SASS train could be improved to about ±25 percent by using a 16-point traverse rather than sampling at a single point.

2) General
   - For traverse sampling, the largest individual error will normally be in collected particulate mass, due to anisokinetic sampling and flow/probe misalignment.
   - System accuracies of ±10 percent to ±16 percent can be achieved using commercially available equipment and a 16-point traverse. These accuracy levels, while not required for environmental assessment, indicate potential accuracies for control device evaluation testing.

It is recommended that:

- The SASS train in its present state is recommended for Level 1 assessment work, using single point sampling. A modified traverse (along a single line) should be considered for places such as ESP outlets to minimize errors due to stratification.
- Additional stratification data should be obtained at sites such as full-scale, coal-fired power plants for the three general types of most important locations: control device inlets, control device outlets, and stacks. Such data should be obtained with a single (or identical) train(s) to isolate the stratification data.
- Development of methodology to optimize single point sampling accuracy through judicious selection of the sampling point should be pursued through analysis of stratification data and proof of principal source testing for proposed techniques.
- There is a need for lightweight, high volumetric flow sampling hardware and associated procedures to perform quick (1-2 hour) surveys to determine particulate stratification in sources so that appropriate techniques can be used for longer term source assessment testing.
- Additional error analysis work should be performed for size fractionating sampling techniques. The present analysis applies only to the total particulate mass determination.
- Although this report does not deal specifically with Method 5 hardware and procedures, results suggest that for hardware of a given accuracy, there will exist specific procedures to optimize system performance (achieve close to maximum accuracy while minimizing manpower requirements and sampling times). Work should be continued to prepare an IERL-RTP Procedures Manual in this area.

2.16 TASK 32 SUPPORT TO LEVEL 1 ENVIRONMENTAL ASSESSMENT STUDY

2.16.1 Objective

Radian Corporation, Austin, Texas, is conducting a Level 1 Environmental Assessment (EA) of a low BTU Coal Gasfication Plant at the Holston Army Ammunition Arsenal. TRW has been assigned by PMB to assist, advise, and instruct Radian in all phases of this Level 1 pilot study.

Four subtasks describe the full scope of Task 32. There are:

Subtask 1. Prior to Field Analysis--

TRW would establish a working relationship with Radian. This working relationship includes an initial home office visit to establish in them a comprehensive understanding of the philosophy, sampling protocols, and equipment required to conduct a Level 1 EA, instruction of Radian's personnel in Level 1 sampling and analytical procedures and determining the extent of a quality assurance program.

Subtask 2. During the Field Analysis--

TRW would provide "on site" sampling and analysis assistance when Radian is in the sample acquisition phase and field analysis phase. This assistance would include, but not be limited to: identification/correction of deviations from the promulgated Level 1 procedures; identification/correction of sampling and/or analytical deficiencies, preparation of a letter report describing problems, solutions, and ease with which the procedures were used.

Subtask 3. Analysis of Samples at Radian's Site--

TRW would follow the analysis of the samples which were acquired. If analysis problems occur, it would be the responsibility of TRW to advise the PMB Project Officer and the EA contractor's Project Officer of the difficulty and obtain concurrence to perform additional analyses on the sample. It is TRW's responsibility throughout the pilot study to assure the EA Project Officers that they will obtain the information which is required.

Subtask 4. Reporting--

At the conclusion of this effort, the contractor will prepare a report which identifies areas that require additional sampling and/or analytical research and development to improve Level 1 procedures. This document will include the ideas of each monitoring contractor who was involved in each pilot study.

2.16.2 Approach

This is basically a consulting task. However, TRW's approach has been to not only aid Radian in their efforts but also to contribute to the overall development of the Level 1 methodology.

2.16.3 Technical Discussion

The major work areas of this Task have been completed. Therefore, the following technical discussion is organized to report sequentially on each subtask described in Section 1.0.

Prior to Field Analysis--

TRW visited Radian's Laboratories with the PMB Project Officer in late March 1977. Key personnel contacts were established and the Level 1 philosophy, sampling protocols, sampling equipment operation, and analytical procedures were discussed in detail with Radian's performing team.

On 15 April 1977 TRW compiled and submitted to PMB a report on the "Problems and Deficiencies, Level 1 Environmental Assessment Procedures". This was to serve as the discussion basis of a meeting held on May 2 and 3 at RTP between the PMB contractors involved in the Level 1 pilot studies (RTI, ADL, and TRW). At that time various modifications were agreed upon and adopted to the Level 1 sampling and analysis protocol. These were:

- Various changes in field GC operations to accommodate particular instrumental differences.
- Gas Sampling Tedlar bags acceptable for gas sampling.
- Adoption of a new sample combination scheme.
- Approval and incorporation of a new organic analysis scheme.

Action items which were assigned to the PMB contractors as a result of this meeting were:

ADL

- Conduct a meeting with the Level 1 pilot study and the PMB contractors to standardize the LRMS procedure and interpretation.

TRW

- Develop a contamination-free Parr Bomb Procedure.
- Investigate and resolve the recovery problems of As, Sb and Hg from the impinger solutions.
- Provide step-wise procedures for As by the silver diethyl dithiocarbamate procedure, Hg by the cold vapor technique and Sb by the Atomic Absorption Spectrometry procedure.

ADL held their coordination meeting in late May and TRW participated. TRW delivered to PMB the developed procedures on 3 June 1977 in letter report form.

During this period letters and telecons with Radian were actively answering the sampling and analytical inquiries and their test plan was reviewed. Arrangements were also made to have a TRW representative present during the field sampling activities.

During the Field Analysis

Radian field test was conducted in August. The TRW representative was present during their Level 1 acquisition phase on August 30 and 31. He participated in decisions concerning modification of the sampling procedures for the high tar content vent sampled. These included but were not limited to:

- The downtime realized for changing of plugged filter. This would result in a longer total sampling time to acquire the Level 1 required $30M^3$. Therefore, it was decided to change the filter as often as necessary and sample as long as possible to acquire a reasonable quantity of sample. Documentation of the exact sampled volume was made.
- High tar condensation was observed in the cyclones. Plugging was also a problem experienced. Two additional problems resulted from this condition. One was the loss of particle size separation and the other was the lack of adequate tar removal by the methylene chloride rinse. It was found that better separation could be achieved without heating the cyclones

and allowing greater tar condensation. This also reduced the plugging problem. Methylene chloride/methanol and mixtures were used for additional tar removal.

Analysis of Samples at Radian's Site --

On November 10th and 11th a TRW representative visited Radian to observe the Level 1 sample analysis phase of the pilot study and assist with problems. Briefly the findings of this visit can be summarized as follows:

- The high tar content prevented analysis to proceed along "particulate" breakdown Level 1 guidelines.
- The high organic, sulfide and cyanide levels in the separator liquid sample produced interferences with several of the field water quality tests and made the odor and alkalinity measurements incapable of being conducted due to health hazards.
- Methylene chloride was found to extract only between 31-35% of the organics present. Other solvent systems, therefore were implemented.
- Fractions 4 through 8 of the liquid chromatographic separation were smeared to the extent that the Infrared Spectroscopy and Low Resolution Mass Spectrometry were difficult to interpret.
- The Gas Chromatographic, TCO, analysis if conducted exactly by the Level 1 procedure was not quantifiable because of extremely high loading on the column.
- Various alternative organic analysis procedures were discussed. These would all be considered "Level 2" in nature. However, the validity of proceeding to Level 2 organic sampling and analysis is well justified from the Level 1 data and proved Level 1 to be viable both in sampling and analysis.

Reporting --

The final documentation on this task was sent at the end of May 1978. Additional reporting requirements have been met with monthly progress reports and letter reports.

2.16.4 Summary of Results and Recommendations

In summary, this task has provided a necessary evaluation mechanism for the Level 1 Environmental Assessment protocol as applied to an unusually high organic content stream. The sampling and analytical insight gained from this test has been valuable to the evolution of the Level 1 methodology. When the test's final evaluation and Level 1 recommendations have been made, documentation will exist to aid future teams in conducting sampling and analysis on similar sites.

This type of team effort can be valuable to future activities. The combination of an EA with a PMB contractor provides an excellent blend of sampling and analytical expertise.

2.17 TASK 36 INORGANIC MEG COMPOUNDS AND LEVEL 1 ASSESSMENT

2.17.1 Objective

This 100-hour task was initiated to theoretically predict:

- If Level 1 Environmental Assessment is capable of detecting the inorganic Multimedia Environmental Goal (MEG) compounds and elements at their Estimated Permissible Concentrations (EPC).
- Where in the Source Assessment Sampling System each inorganic compound and element is likely to be found.
- What MEG compounds, elements and valance states can be predicted in Level 1 aqueous samples.
- The nature of difficulty in detecting by "non-Level 1" techniques MEG compounds at EPC levels.

Organometallic MEG compounds were not included in this study.

This basic study was completed in June 1977. The task was reopened to address the current list of MEG compounds (November 1977) at their Minimum Acute Toxicity Effluent (MATE) levels. The draft document issued in June 1977 was revised using MATE's in place of EPC's.

2.17.2 Approach

Two general approaches were taken. One was to theoretically discuss the capability of Level 1 to detect the MEG compounds and elements at their EPC concentrations. The other was to assess actual Level 1 data and compare values obtained and limits of detection with the EPC's.

2.17.3 Technical Discussion

The theoretical discussion which predicted the capability of Level 1 to detect MEG compounds at their EPC concentrations simply back-calculated from the EPC's the probable quantity present in a $30M^3$ sample (EPC concentration in $\mu g/M^3 X\ 30M^3$). The effects of SASS distribution and sample combinations, preparation, and the specific analytical techniques detectability were then considered. Based on these predictions most of the inorganic elements at EPC's were detectable by the Level 1 analytical techniques. Problem elements, because of the Level 1 factor of 3 accuracy, were identified.

A discussion of SASS distribution based on actual run data was also part of the approach. Through the knowledge of concentration levels of MEG compounds probable in common sources, and comparison of these actual values and actual limits of detection with the EPC's, problematic MEG compounds were identified. In general, detectability problems (at the time of this original study) at coal- and oil-fired plants had not been encountered.

The investigation of Level 1 water samples considered the MEG inorganic compound's physical properties and predicted the probable MEG species present based on solubility and stability. The MEG inorganic elements were also tabulated comparatively with the detection limit for each element in water by SSMS and the Level 1 wet chemical techniques. Level 1 was found to be viable for most MEG's with problems possible when EPC levels of Be and As are sought because of the Level 1 accuracy requirements.

The "non-Level 1" techniques recommended for the detection of problematic MEG compounds and elements were:

- Sample concentration by a factor of 10(100 mL to 10 mL)
- Graphite Tube Atomic Absorption Spectroscopy (AAS)

2.17.4 Summary of Results and Recommendations

The results and recommendations from the "Draft on Inorganic MEG Compounds and Level 1 Assessment Detection Capability" (Document #28055-6008-TU-81) dated 30 June 1977 were as follows:

Conclusions--

- The Level 1 Environmental Assessment protocol is capable of detecting most MEG elements at the concentration levels imposed by the EPC X 100 criteria.
- Beryllium at the EPC X 100 level of interest is theoretically not detectable by current Level 1 techniques.
- Arsenic, selenium, thallium, chromium, silver, lithium, antimony and cadmium are theoretically not detectable at the EPC X 100 level of interest in some of the SASS components.
- Detectability problems have not yet been encountered for MEG elements at coal-and oil-fired systems sampled.
- In water samples, beryllium and arsenic at EPC X 100 levels of interest are not detectable by current Level 1 techniques.

Recommendations--

- Investigate the recovery, detection limits and costs of analyzing Be, As, Se, Th, Cr, Ag and Cd standards at the predicted EPC concentrations, by the graphite tube atomic absorption spectroscopic technique after a sample concentration procedure.

Recommendations were also made to revise this draft document using MATE concentrations in place of the EPC, and it was completed in May 1978.

2.18 TASK 42 SUPPORT SERVICES TO LEVEL 1 ENVIRONMENTAL ASSESSMENT PERFORMANCE EVALUATION

2.18.1 Objective

The objective of this recently completed task was to support TRW's participation with RTI, ADL, Radian, and SoRI in collaborative testing of the SASS and the Level 1 analysis procedures. The purpose of the overall test program was to define the precision of the Level 1 procedures.

2.18.2 Approach

The effort consisted of two verification phases. Phase I involved a field sampling effort in which SASS performance and field procedures were evaluated. Field sampling teams from Radian, SoRI, and TRW participated in the Phase I effort which was conducted at an aluminum smelter. The collaborative sampling effort involved the use of three trains (two SASS and one method 5) during three sampling runs. This matrix allowed the rotation of the trains such that each participating team used each train once.

Phase II involved a similar collaborative effort directed at the Level 1 laboratory analysis procedures. Three types of samples were prepared by ADL, one of which was directly derived from the samples acquired in Phase I, and the other two were specially compounded with known mixtures. Only RTI, who acted as the central study coordinator, was informed by ADL of the composition of the specially prepared samples. All analyses were conducted in strict accordance with procedures as specified in the EPA-IERL Level 1 manual. The only instances involving modifications or deviations from the Level 1 manual were when newly revised, EPA approved procedures superceded them. These new procedures were documented by RTI and supplied to all contractors participating in this study.

2.18.3 Technical Discussion

The collaborative sampling matrix involved the use of three trains (two SASS and one method 5), rotated in such a way that each contractor used each train once. This rotational matrix is illustrated by the following example:

	SASS 1	SASS 2	Method 5
Test 1	SoRI	RADIAN	TRW
Test 2	TRW	SoRI	RADIAN
Test 3	RADIAN	TRW	SoRI

In the performance of this phase of the task, TRW not only supplied a sampling crew but also:

- Acted as key contact with Kaiser Aluminum to arrange schedules and logistics for the sampling effort.
- Performed a pre-test site survey.
- Arranged for the installation of sampling ports.
- Supplied one of TRW's mobile source assessment vans equipped to perform on-site weighings, GC analysis, and general Level 1 support.

The results of the Phase I efforts were recorded and reported by RTI. RTI also coordinated the Phase II analytical testing, collected all data from the participating contractors, and is in the process of preparing a report on the collaborative results.

TRW supported the Phase II effort by analyzing the selected samples provided by RTI (prepared with the support of ADL). These samples were submitted to the standard Level 1 scheme in routine use by TRW on the "Environmental Assessment of Conventional Combustion Systems" program, and all results along with copies of raw data were reported to RTI.

2.18.4 Summary of Results and Recommendations

Although remarkable progress has been made toward defining the details of the Level 1 procedures in the relatively short period of time since they were first published, there remain considerable ambiguities which can lead to differences in the interpretation of the procedures. That such differences exist was evident in both phases of the effort. The seriousness of these potential interpretive differences will hopefully be addressed in RTI's summation of this collaborative testing.

As a result of an ongoing project at TRW involving the environmental assessment of stationary combustion sources, a detailed, highly specific rendition of the Level 1 procedures has been written. This document is called the "Emission Assessment of Conventional Combustion Sources Procedures Manual for Sampling and Analysis" (EPA Contract 68-02-2197) and is written in a format which is amenable to standardization and which has been successful in its implementation. It is thus recommended that a similar, detailed format be used in the revised publication of the Level 1 procedures. Using this kind of format there can be very little doubt as to specific procedural directives.

2.19 TASK 47 AUTOMATIC SULFUR TRIOXIDE MONITOR

2.19.1 Objective

The objective of this task was to develop an automatic sulfur trioxide monitor based on the Goksoyr-Ross coil capable of providing reasonably accurate measurements (±20%) of sulfur trioxide concentration in process gas streams. The unit was to be designed for continuous, unattended operation for periods on the order of 24 hours.

2.19.2 Approach

The task was divided into the following items:

- Design of the prototype unit
- Construction and laboratory tests
- Field test evaluation
- Preparation of final report and operations manual

The unit was designed with the idea of facilitating field handling, and for ease of operation. The final design was submitted to IERL/RTP and work began on construction of the prototype unit. The hardware buildup was aimed specifically at providing a unit capable of operation in a field environment, thereby necessitating sturdy construction. The unit was designed to be easily modified if necessary, and had an extremely flexible control system installed.

The laboratory tests and field tests will be performed to determine the monitor's performance capabilitites, particularly under actual field conditions. Upon successful completion of these tests an operations manual with the system's description will be written, as well as a final report summarizing the test results.

2.19.3 Technical Discussion

The monitor was designed in two units; the probe unit which contains the glass sampling train and conductivity cell (Figure 25) and the control unit, which contains the automatic sequencer, electrical distribution panel, and pumps. The sampling train was designed of all pyrex or quartz, and the solenoid valves utilized were of all Teflon construction so that

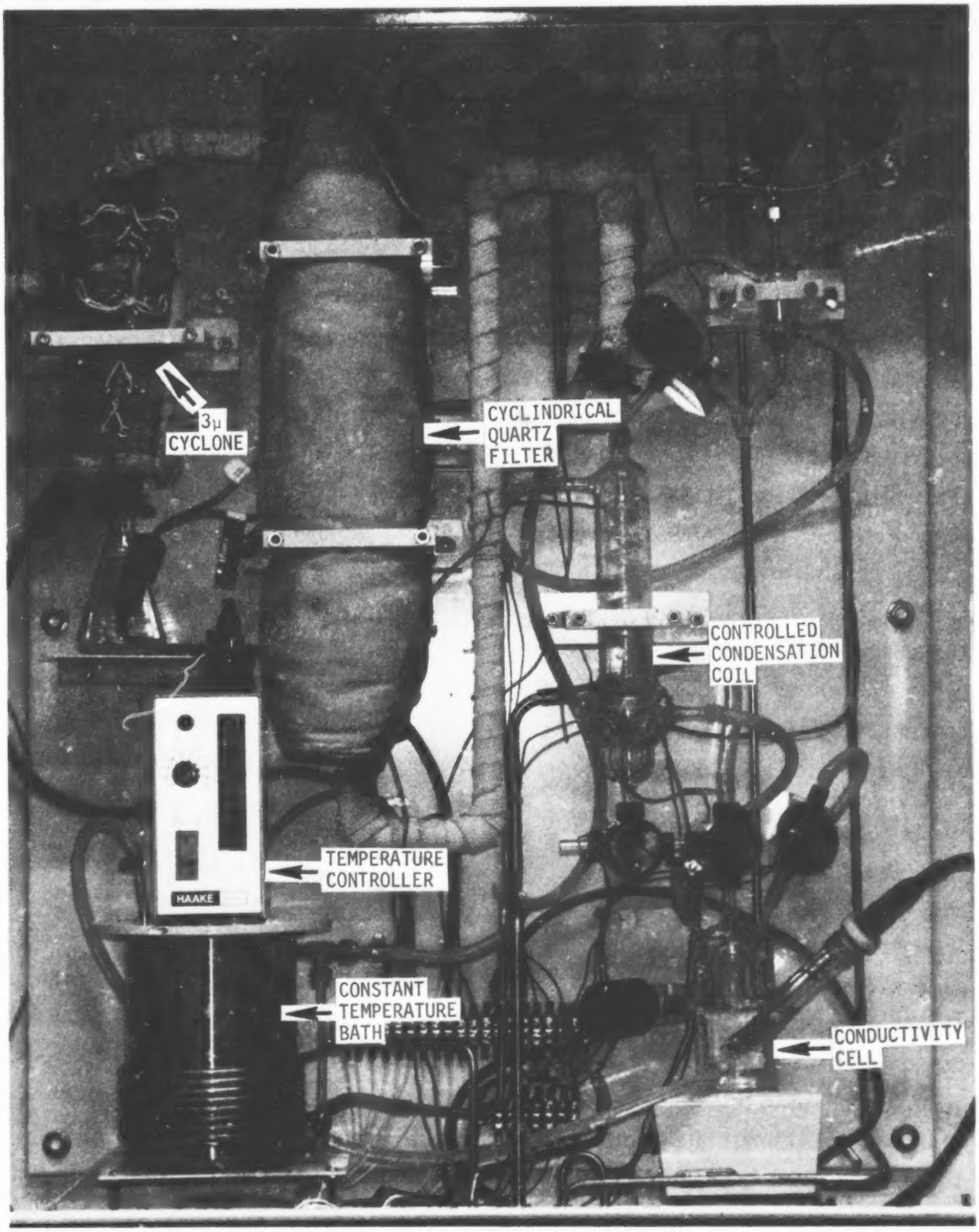


Figure 25. Inside View of Automatic SO_3 Monitor

the acid solution would not contact any metallic components. The function of the monitor's components are controlled by a sequencer which has eleven separate timing channels, each variable from 0 to 999 seconds. The sequencer operates the components in specific cycles according to the sampling time desired. The output of the unit is in terms of solution conductivity; a conductivity cell measures the conductivity of a rinse solution which has washed through the Goksoyr-Ross coil, thereby providing data on the amount of acid in the solution. Through calibration, this can be related to sulfur trioxide concentration in the sample gas.

A series of engineering sketches was prepared showing the design of each major component in the two units, and a complete list of parts and suppliers was submitted to IERL/RTP. The control system was of considerable importance and therefore a considerable amount of time was devoted to its design and construction. Versatility and ease of timing alteration were of prime importance. The sampling system components were manufactured of quartz and/or pyrex in order to withstand the temperature and acid solution without degradation. The entire sampling system from probe inlet to the controlled condensation coil is heated to 288°C to prevent acid condensation prior to the coil. All components necessary for the measurement of conductivity are water-jacketed at 60°C ± 1°C to provide temperature stability. This is essential for accurate conductivity measurements.

2.19.4 Summary and Conclusions

The field test unit has been successfully operated both in the laboratory and in the field at the Tennessee Valley Authority Shawnee Power Plant. The probe unit itself weighs 41 kg and is 91 x 76 x 30 cm in overall dimensions. The glassware components are firmly mounted with shock-reducing mounts to reduce stress on the glass in field operation. The control unit components are temporarily mounted in an electronic enclosure for the laboratory tests. Connections to the probe unit are a series of quick disconnect fittings and thermocouple jacks. This facilitates set-up in the field since both units are self-contained.

Laboratory testing showed the monitor capable of a linear response to sulfuric acid concentrations as low as 0.5 ppm during a 7 minute sampling cycle, with variations in conductivity output of ± 4%. Smaller concentrations may be detectable within this accuracy by increasing the length of the sampling cycle. Tests utilizing a sulfuric acid mist generator at the probe inlet showed that the system recovers 92% of the acid injection. Variations in system performance at the extreme range of conductivity measurable indicated an accuracy of ±9% under laboratory conditions. The system was also shown to be unaffected by SO_2 in as high as 4000 ppm concentration. All tests were performed with the system operating in the fully automatic mode to duplicate field conditions as closely as possible.

A one-week field test was performed at the Shawnee facility. No problems were encountered in setup of the equipment; however, the sampling probe and replacement were destroyed in shipment. Initial tests were begun using a repaired probe while new probes were being prepared. A continuous test of 3.75 hours in duration was performed at the inlet to the venturi-scrubber, where high particulate loadings were encountered (11 g/m^3). During this test, it was necessary to add an impinger and absorber to remove condensed water from the vacuum lines. This water vapor damaged the differential pressure meter so that a dry gas test meter was added to obtain an accurate gas flow reading. Manual samples were taken with a manual Goksoyr-Ross system to provide reference data; the measurements agreed within ±7% at 20 ppm concentration.

Due to shutdown of the scrubber being sampled, the equipment was moved to the inlet of a second scrubber. An endurance test was started with a new probe and clean filter and condensation coil. During a 12-hour continuous run, measurements with the automatic system agreed with spot measurements taken with the manual system within ±4% at 8 ppm.

A problem occurred which prevented longer continuous tests. It appeared that a heavy oily substance was being condensed and trapped on the condensation coil frit, thereby plugging it and stopping the monitor's operation. Subsequent tests with a new condensation coil provided only 2 hours more of continuous operation.

The results of the successful laboratory and field tests were documented in a final report submitted in September 1978. A comprehensive Operations and Maintenance Manual was also prepared.

2.20 TASK 48 ANALYSIS USING ION CHROMATOGRAPHY

2.20.1 Objective

The task was devoted to the development of an analytical scheme utilizing ion chromatography to determine specific ions in dual-alkali process streams. The goals of the task were to: develop a sample collection plan; develop a sample preservation plan; develop a separation procedure for solution, slurry, solids, and solubles in cake; demonstrate the accuracy and precision of the analytical scheme; and write an analytical procedure manual.

2.20.2 Approach

Sampling programs were prepared for a venturi/spray tower (limestone) scrubber and a pilot dual alkali scrubber. These two types of scrubbers were selected because they are representative of current technology and future technology. The specific facilities finally chosen were the Tennessee Valley Authority (TVA) Shawnee Test Facility, Paducah, Kentucky, and the Arthur D. Little pilot dual alkali scrubber.

Working both with samples from the Shawnee facility and with synthetic mixtures, procedures were established to preserve samples, separate liquids from solids in the field, and to accurately and precisely analyze the samples for the species of interest: sulfate, sulfite, chloride, carbonate, nitrate, calcium, magnesium, sodium, and potassium.

2.20.3 Technical Discussion

A sample preservation plan was developed for a typical dual-alkali wet scrubber process. Samples from the process streams are separated into two groups, solids and solutions. Solution samples and filtrate from slurry samples are further divided into five groups and preserved on site according to Table 23. Solid samples, solids from slurry samples and filter cake samples are not preserved but just placed into containers. These actions ensure that equilibria between species in these samples are preserved whenever it is necessary. Preservatives and holding times are specified to prevent deterioration of species susceptible to chemical changes.

TABLE 23. RECOMMENDATIONS FOR SOLUTION PRESERVATION

Measurement	Container	Preservative	Holding Time
Total oxidizable sulfur Sulfate Hydroxide Acidity Carbonate Chloride	Plastic	Cool, 4°C	24 hrs
Calcium Sodium Magnesium	Plastic	HNO_3 to pH 2	6 mos
pH	Plastic	Cool, 4°C Detection on site	7 hrs
Total Sulfur	Plastic	Cool, 4°C Zn Acetate	24 hrs
Nitrate	Plastic	Cool, 4°C H_2SO_4 to pH 2	24 hrs

A separation procedure for solution, slurry, solid and solubles in cake was developed. The separation procedure is divided into two parts: liquids sample and solid samples. Slurry samples will be filtered and solids which pass through the 0.5μ Fluoropore filter will be considered in solution.

The recommended filter is 0.5μm Gelman Acupore. Acupore filters are both chemically clean and inert to most organic and corrosive solvents. Furthermore, Acupore does not have a tendency to absorb metals on its surface. If a slurry sample is found to contain a large amount of solids, pre-filtration is necessary using another Teflon filter, Millipore Mitex. This filter is available in a 10μ-pore size and is designed to act both as a membrane and depth-type filter. The larger pore size of the Mitex filter allows for a higher solid content without clogging. Pre-filtration with Mitex followed by filtration through 0.5μm Acupore should produce a solids-free solution.

Solid samples will be dissolved in concentrated nitric acid and the resulting solution or slurry will then undergo the same treatment as the liquid samples.

The analytical scheme for anion analysis had to overcome two major problems: NO_3^- and SO_3^{-2} ions had very similar retention times, and CO_3^{-2} ions could not be detected in the presence of the anions of interest because $CO_3^=$ ions were part of the eluent solution. In order to determine all the anions of interest in a sample, the anion sample would have to be run three separate times on the ion chromatograph using two different sets of columns.

The analytical scheme for anion analysis finally developed involves these basic procedures:

1. The first anion sample run determines the amounts of chloride, total oxidizable sulfur (TOS), and sulfate. The columns employed in the ion chromatograph are the Dionex anion separator and suppressor with a $Na_2CO_3/NaHCO_3$ solution as the eluent.

2. The second anion sample run determines the concentration of nitrate. The ion chromatographic columns and conditions are the same except that the anion sample is pretreated with H_2O_2. The peroxide provides two services: it oxidizes the sulfur in the solution to $SO_4^=$ so that the total sulfur can be determined in the sample; it oxidizes $SO_3^=$ to $SO_4^=$ thus deconvoluting the $SO_3^=/NO_3^-$ peak overlap.

3. The third anion sample run determines the amount of carbonate. the ion chromatograph is set up with a BioRad AG 50W suppressor column and water is the eluent. The single suppressor separates the $CO_3^=$ ions from all other anions.
4. Hydroxide can not be determined by ion chromatography. Alternative approaches to the hydroxide problem are acid/base titration or pH determination.

In the analytical scheme for cation analysis, calcium, magnesium, and sodium were separated and detected by ion chromatography with a Dionex separator and suppressor column. Calcium and magnesium were separated with a p-phenylenedramine dihydrochloride eluent while sodium was separated using a nitic acid eluent.

The analytical scheme for cation analysis can be summarized as follows:

1. The first cation sample run determines the amounts of sodium. The columns employed in the ion chromatograph are the Dionex cation separator and suppressor with a HNO_3 solution as the eluent.
2. The second cation sample run determines the amount of calcium and magnesium. The same type Dionex cation columns are used as in Step 1, but a p-phenylenediamine dihydrochloride solution is the new eluent. Two separate sets of Dionex cation columns must be employed for cation detection because p-phenylenedramine dihydrochloride tends to degenerate the column packing material and this would cause an interference with the sodium separation. The nitric acid eluent for sodium does not separate the calcium and magnesium.

Table 24 lists retention times and corresponding operating parameters of the various ions present in wet scrubber samples.

The accuracy and precision of the analytical scheme was tested using real samples from the lime/limestone wet scrubber at the TVA Shawnee Plant in Paducah, Kentucky. Table 25 shows a direct comparison between TVA and TRW sample analysis for the lime/limestone wet scrubber. Because the values reported for magnesium and sodium varied greatly, the samples were determined a second time by atomic absorption at TRW and these new results were in line with the ion chromatography values. These results indicate that there must be a shift in the solution equilibrium because of the time difference between sampling at Paducah and analysis at TRW. A check of the pH of the sample solutions showed that all the solutions decreased in acidity to almost neutral or basic. A shift in pH would account for the differences in the magnesium concentration reported because magnesium oxide is only slightly soluble in solution. On the other hand, the chloride

TABLE 24. RETENTION TIME OF VARIOUS IONS FOUND IN WET SCRUBBERS

Species	Conc.	Retention Time	Dionex Separator Column	Dionex Suppressor Column	Flow Rate	Eluent	Temp.
Cl^-	10 ppm	4.5 min	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
$SO_3^=$	10 ppm	10	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
NO_3^-	10 ppm	8	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
$SO_4^=$	10 ppm	16	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.0025M Na_2CO_3	24°C
CO_3	10 ppm	6	BioRad 6 x 500	None	30%	Water	24°C
Ca^{+2}	10 ppm	12	Cation 6 X 250	Cation 9 x 250	40%	For both Cations 0.001 M p-phenylene-diamine dihydrochloride	24°C
Mg^{+2}	10 ppm	8	Cation 6 x 250	Cation 9 x 250	40%		24°C
Na^+	10 ppm	7	Cation 6 x 250	Cation 9 x 250	40%	.005N HNO_3	24°C
K^+	10 ppm	12	Cation 6 x 250	Cation 9 x 250	40%	.005N HNO_3	24°C

TABLE 25. DIRECT COMPARISON BETWEEN TVA AND TRW SAMPLE ANALYSIS FOR THE LIME/LIMESTONE WET SCRUBBER.

Species	Method of Analysis	Concentration (in ppm) TVA Sample Identification			
		#5253	#5254	#5255	#5256
Calcium	Atomic Absorption (TVA)	604	624	618	667
	Ion Chromatography (TRW)	551	618	614	541
Magnesium	Atomic Absorption (TVA)	8219	5269	4629	8179
	Ion Chromatography (TRW)	10506	5030	5536	10014
	Atomic Absorption (TRW)	11025			10490
Sodium	Atomic Absorption (TVA)	186	192	55	47
	Ion Chromatography (TRW)	172	197	99	92
	Atomic Absorption (TRW)		195	102	
Sulfate	Ion Exchange (TVA)	32994	17584	17700	31442
	Ion Chromatography (TRW)	34000	16209	16660	34404
Chloride	Potentiometric (TVA)	2676	1418	1418	2614
	Ion Chromatography (TRW)	2726	1454	1485	2675

concentration would not be susceptible to changes in pH, and this was confirmed by the good correlation between the TVA and TRW values. Sodium ion concentration should not vary with changes in pH but only two of the four TVA determinations showed good agreement with the TRW results. The two values which disagree are approximately one-half less than the TRW values and this could be accounted for by a dilution factor mistake or a calibration mistake on the AA. Sulfate ion concentration would constantly increase with time because any sulfite present would oxidize to sulfate. The TRW values for sulfate show both high and low values compared to the TVA results but both sets of analysis still show good agreement. The variations between the TVA and TRW sample analysis seems to be due to sampling and time between analysis and not an instrumental problem.

2.20.4 Conclusions

The results of this work have been compiled in a procedures manual, "Chemical Analysis of Wet Scrubbers Utilizing Ion Chromatorgraphy," which describes how to collect and preserve samples as well as how to perform qualitative and quantitative analysis for sodium, potassium, magnesium, calcium, chloride, TOS, sulfate, sulfur, nitrate, carbonate and hydroxide.

2.21 TASK 49 MASS EMISSIONS MONITOR DEMONSTRATION

2.21.1 Objective

The principal objective of this task was to demonstrate hardware and methodology for continuous high accuracy flow and gas composition measurement in large stationary source ducts and stacks. The technology being demonstrated was developed under previous EPA sponsored programs, and showed the potential for large accuracy increases over single point continuous sampling techniques without a substantial system cost and maintenance impact. The technology also has the capability to be used for active process control in addition to passive monitoring.

2.21.2 Approach

The gas sampling portion of the system differs from current continuous extractive sampling practices only in that a special (patented) type of multiple point gas sampling probe is used. The probe has a single outlet, and so is quite similar in use to a standard single point gas sampling probe. In the preferred approach, volumetric flow is measured by means of a Dieterich Standard Annubar, which is a kind of multiple point pitot probe with a single differential pressure as the output. Since the specialized equipment being demonstrated was "front end" hardware, the approach taken was to find a location where a full sampling system was in operation and then perform the task by substituting our probes, so that we could made use of the rest of the system (sample lines, gas conditioner, analyzers, recorders, etc.). The only identified site at which we could do this was the NIPSCO coal fired power plant in Gary, Indiana, where TRW's Environmental Engineering Divison was running a demonstration test on a novel type of wet scrubber. An agreement was negotiated whereby our stack gas sampling probe would be substituted into their system, and we would make use of Annubars already installed in the stack. In addition, we would supply a separate system upstream of the scrubber to measure volumetric flow and bulk gas composition (N_2, CO_2, O_2). The test period was planned to be two weeks in a "hands-off" mode.

2.21.3 Results

The field effort was for the most part unsuccessful. The scrubber was down for repairs during most of the test. At this particular site, that meant that the flue gas was diverted to another stack, so that stack measurements could not be obtained. A few days before the scrubber came back on, the EED sampling system broke down and was down for the remainder of the test. No stack measurements were obtained, even though the test period was lengthened by a week in anticipation of the scrubber coming back on line.

At the upstream location, volumetric flow data had to be recorded manually due to a malfunction in our printer. Excessive flue gas temperatures led to an early failure of the multiple point gas sampling probe. The one significant observation made during the test came from comparisons of continuous single point data from our upstream location and from an EED monitoring location further downstream. Systematic shifts in gas composition measurements at the two locations revealed the presence of significant compositional stratification, the problem the multiple point probe was designed to handle.

2.21.4 Recommendations

The observed presence of significant compositional stratification at the test site reinforced the need for further work in the area of high accuracy continuous monitoring.

2.22 TASK 51 EPA/TVA LIMESTONE FGD SUPPORT

2.22.1 Objective

The task was devoted to supporting process measurement activities at the EPA/TVA Shawnee Wet Limestone Test Facility in Paducah, Kentucky. The initial tasks were devoted to the investigation of trace element vs particle size distribution and liquid aerosol sampling of flue gas streams. The investigation involved study of: stack samplers and particle sizing; basic theory, limits of detection, limitations and cost of multielemental analytical instrumentation; instrumentation for compound identification and surface analysis; liquid aerosol sampling.

2.22.2 Approach

The principal topics of concerns requiring technical support have been

1) recommending particle sizing and trace elements analysis approaches
2) reviewing and recommending sampling techniques and analysis methods for trace element and compounds
3) recommending sampling procedures to identify sulfur forms
4) evaluating the feasibility of sampling liquid aerosols at a mist eliminator
5) developing automated methods to measure scrubber process stream parameters and thereby improve control of the scrubber operation.

Each has been discussed either at a symposium or in a carefully researched report.

2.22.3 Technical Discussion

Trace Element Sampling and Analysis --

A report consisting of four sections was written discussing stack samplers, trace multielemental analysis instrumentation, instrumentation for compound identification, and recommended combinations of stack samplers and analytical instrumentation. A variety of sampling equipment for flue gas particle sizing were discussed, including an: Aerotherm high volume stack sampler, an Aerotherm source assessment stack sampler, and a Meteorology Research, Inc., Impactor (Model 1503). A brief discussion of the basic theory behind the trace elemental analytical techniques, including limits of detection, lists of limitations and analysis costs for Atomic Absorption Spectroscopy, Spark Source Mass Spectrometry, Inductively Coupled Plasma Optical Emission, Neutron Activation Analysis, and Proton Induced X-Ray Emission was given, as was a brief description of the instrumentation necessary for compound identification and surface analysis: X-Ray Powder Diffraction, Scanning Electron Microscope, Electron Probe Microanalysis, Secondary Ion Mass Spectrometry, and ESCA/Auger.

Sulfur Form Sampling and Analysis--

A document was prepared which describes how the controlled condensation system can be modified to collect sulfate particles, H_2SO_4, SO_2, HCl and HF. Recommended analytical procedures were included.

Liquid Aerosol Sampling--

The task was to measure the mass flow and size distribution of water droplets at the inlet and outlet of mist eliminators at the TVA Shawnee Wet Limestone Test Facility.

The following stream characteristics were considered representative:

T: 50°C
Droplet Loading: of order 2-20 grains/SCF at inlet
0.02 grains/SCF at outlet
Gas Velocity: 2.5 - 3.5 m/s at inlet
18 m/s at outlet
Humidity: 100% + droplets
Inlet: 2.5 m diameter.

The water content of saturated air @ 50°C was approximately 45 grains/SCF, and a 1°C change from 50°C altered the water content by about 2.5 grains/SCF. This means that any measurement technique would have to be highly isothermal in order to avoid altering the raio of liquid to gaseous water, which would result in a meaningless measurement. Thus, any extractive technique would not be feasible. Two approaches to the problem were considered. The first, an in situ optical approach, was eliminated because a suitable optical measuring device is not now commercially available. The second approach was droplet counting and sizing by means of a hot wire or hot film sensor.

Hot wire sensors have long been used in gas flows and in liquid flows for velocity and turbulence measurements. It has more recently been verified that hot-wire sensors can be used in two-phase flows (liquid droplets dispersed in a gas) to measure droplet size. Fortunately, the droplet size range in which the approach is practical is also the droplet size range of interest for this specific problem. As a droplet contacts the heated wire, it is captured through surface tension forces and remains attached to the wire. It then evaporates, leaving the wire bare and "ready" for the next droplet impact. The evaporation phase, for normal operating conditions, lasts from one to ten milliseconds, according to the size of the initial droplet. The wire is heated by means of an electric current to a specified temperature above ambient. When a droplet at ambient temperature strikes the wire, the increased heat transfer rate causes an increase in the amount of current required to maintain the specified temperature (referred to as overheat temperature). The current increase is actually measured as a voltage increase. The droplet impact produces a voltage spike (typical rise time to maximum voltage 0.1 msec), with the voltage dropping back to its undisturbed value as the droplet evaporates. This peak height has been observed to be a linear function of the droplet diameter.

The KLD Model DC-1 Droplet Counter is a commercial device specifically designed to use a hot-wire sensor in the manner described above to measure "the size and concentration of water droplets present in the stream of scrubbers." It does have to be used conscientiously to get valid results, especially with the higher gas velocity of the outlet. Several comments, not in the operating manual, which could improve data follow:

- The instrument output is number of counts per unit time for a specified size range. This immediately gives size distribution at the sampling point, but total mass loading also requires knowledge of the effective wire capture area, which is greater than the wire cross-sectional area, and is a function of particle size. This type of information should be supplied by the manufacturer. Mass balance data comparisons are probably the best way to check the instrument data accuracy, and droplet mass flow, rather than size distribution, is needed to do mass balances.

- It is essential that sampling locations be chosen so that the local droplet velocities are in the same direction as the local gas velocity, the local gas velocity direction is known or can be determined, and the probe can be accurately aligned with the wire axis normal to the flow direction. Alignment of the wire axis normal to droplet direction of motion is required for accurate, meaningful data.

- When droplets evaporate, any solids will be left as a residue on the wire. In a scrubber, of course, significant solids content must be expected. Any residue will act as a thermal insulator and degrade the accuracy of the data. This means that: 1) run times should be kept short to minimize deposition; 2) the sensor should be properly cleaned between runs; 3) it must be realistically expected that there will be run-to-run calibration shifts. These must be accounted for both in operation and data reduction.
- The factory should be consulted on how to get meaningful data at gas velocities as high as 18 m/s, since the instrument specs list a maximum gas velocity of 3 m/s.
- High droplet stratification levels must be expected. Data should be acquired through sixteen-point traverses.

Automating Control of Wet Scrubber Systems--

As a result of a meeting of representatives of EPA, TVA, TRW, Bechtel Corporation and the University of Cincinnati, all of whom are concerned with measuring key process stream parameters and developing control strategies for wet limestone scrubbers, TRW investigated the following questions:

- Evaluate state of the art on-line coal sulfur monitors.
- Investigate pH electrode systems which will withstand on-line conditions in scrubber liquors. (This subtask resulted in the issue of a task to study pH and chloride electrode operation in wet scrubbers. A report of this work is contained in Task 62).
- Investigate non-conventional approaches to monitoring a variable which accurately reflects pH.
- Conduct a literature survey for state of the art FGD monitor systems to see what species are monitored by what methods. Specifically, approaches to real time monitoring of S in coal, gas flow, SO_2, pH, $CO_3^=$, $SO_3^=$, $SO_4^=$, Cl^-, Mg^{+2} and Ca^{+2} should be considered.

2.22.4 Recommendations

Recommendations were made in written reports on equipment and procedures which would be best suited to a particular sampling and analysis problem.

For trace element sampling and analyses, taking samples with the source assessment stack sampling (SASS) train and analyzing them by inductively coupl plasma optical emission spectrometry (ICPOES) will provide the best overall performance and be the most effective. The MRI impactor provides the most size information, but it is limited in sample size and does not collect volatiles.

At this time, liquid aerosol sampling at a mist eliminator is practical only with the careful use of the KLD Model DC-1 droplet Counter.

2.23 TASK 53 INPUT TO LEVEL 1 MANUAL REVISION

2.23.1 Objective

This task was initiated in November 1977, to provide updated and revised chapters on gas, vapor and particulate sampling, and inorganic analysis (Chapters II, III, and VII). These revised chapters were submitted to Research Triangle Institute (RTI) to be incorporated into the upcoming republication of the IERL-TRP Procedure Manual for Level 1 Environmental Assessments.

2.23.2 Approach

The revised chapters provided by TRW were the product of three primary sources of methodology:

1. The current IERL-RTP Level 1 manual (EPA-600/2-76-160a)
2. Procedure modifications that have been compiled by RTI and approved by PMB
3. The detailed and complete Level 1 sampling and analysis procedures manual produced by TRW for use on the Environmental Assessment of Conventional Combustion Sources (EACCS) project.

The approach was to start with the current IERL-RTP manual, incorporate the approved modifications from RTI, and then flesh-out ambiguous and overly-terse areas with diagrams and descriptions from the EACCS manual.

2.23.3 Technical Discussion

The revised chapters submited under this task represented the best currently available Level 1 methodology. Specific tasks conducted on both the TLE and EACCS projects examined and improved the inorganic analysis procedures, and the over 50 Level 1 source tests performed on the EACCS project provided practical experience in dealing with the requirements and realities of field testing. These experiences in both the analytical and sampling aspects of Level 1 methodolgoy had been integrated into the EACCS procedures manual as they evolved. With this task, these improvements have also become part of TRW's input to the revision of the IERL-RTP Level 1 manual. For example, analytical studies have led to the development of the quartz-lined Parr bomb procedure and siginificant refinements to the Hg, As, and Sb procedures to improve sensitivities and counteract problems encountered with the matrix of certain types of Level 1 samples (e.g. peroxide and persulfate impinger solutions).

2.23.4 Summary of Results and Recommendations

The revisions of Chapters II, III and VII vere submitted in March 1978 and accepted by RTI for publication. (The second edition of the manual was issued in October 1978 as document number EPA-600/7-78-201, PB 293 795).

2.24 TASK 57 AT-SEA ENVIRONMENTAL IMPACT STATEMENT STUDIES

The objective of this task was to prepare portions of an environmental impact statement for at-sea incineration of industrial wastes documenting the effects on the environment which could result from the adoption of international standards regulating incineration at sea activities.

The results of this effort were presented to the International Maritime Consultative Organization at their June 1978 conference in London. The final report was published in August. Background information on incineration at sea included a brief history of European and U. S. activities, a projection of the type and quantities of U.S. wastes which might be incinerated at sea, a summary of proposed actions for construction of a U.S. incineration ship, and a listing of U.S. legislation and regulations for controlling incineration at sea.

In discussing the environmental impact of at-sea incineration of organochlorine wastes, special attention is given to the problems of handling hazardous wastes, i.e., potentially carcinogenic, mutagenic or teratogenic substances, wastes containing metals and solid wastes. Incinerator efficiencies and incinerator flame temperatures observed in successful burns on the M/T Vulcanus are also given. Effects on the air quality and water quality from emissions of HCl, unburned wastes and metals are also based on data obtained during actual burns on the M/T Vulcanus.

Disposal of organochlorine wastes by at-sea incineration is expected to have only minimal socio-economic effects. Included in the discussion were specific impacts on beach and shoreline recreation, recreational uses of areas containing the burn zone, demographic impact, economic impact, land use, and required public services.

Three alternatives to incineration at sea are reviewed: secure landfills, land-based incineration and waste recovery by chlorolysis. A section on adverse environmental impacts which are unavoidable particularly points out the risks of accidental spillage. Finally the report included a statement about the commitment of physical and biological resources which is irreversible and irretrievable.

2.25 TASK 62 pH AND CHLORIDE SENSITIVE ELECTRODES

2.25.1 Objective

The goal of this study was to determine the applicability of chloride and pH electrodes in automated control systems. Included in this study was a survey of chloride and pH electrode use in different flue gas desulfurization (FGD) systems and an evaluation test of an industrial pH electrode system.

2.25.2 Approach

The study incorporated a survey of 8 companies utilizing pH and chloride measurements. The methodology and more important, the utility of the measurements were evaluated. When the utility of either electrode's measurements was judged necessary for the majority of the surveyed companies, an evaluation test of the appropriate electrode was to be planned. The purpose of the evaluation test was to determine the applicability of the electrode(s) in automated control system. The criteria for evaluation were in the areas of maintenance, maintenance schedule, accuracy, precision, reliability, and durability. Of these criteria maintenance was the most critical factor.

2.25.3 Technical Discussion

Uses of Chloride and pH Measurements --

Results of the 8 companies surveyed are presented in Tables 26 and 27. The following paragraphs highlight the most significant comments received.

High chloride concentrations (as HCl) may cause internal FGD unit corrosion. Of the companies surveyed only two had reported high chloride levels and made routine chloride measurements in the laboratory on grab samples as a part of the normal FGD unit maintenance schedule. The integration of a chloride electrode into an automated system is only necessary where high chloride concentration is a problem. The applicability of the electrode for automation may take two directions. In one method, chloride measurements are used as a warning device such that operators are notified of high concentration levels and manual operations are used to correct the situation. The alternate approach is to completely integrate chloride measurements into an automated system such that high concentrations will be automatically corrected by the control devices.

TABLE 26. SURVEY OF FGD UNITS FOR pH MEASUREMENTS

UTILITY	KEY CONTACT	CHEMISTRY OF SCRUBBER	COMMERICAL pH MEASUREMENT SYSTEM	LOCATION OF pH ELECTRODES & pH VALUES
1. Shawnee, EPA/TVA Paducah, KY	Gina Dallabetta (415) 768 3567	Limestone	Uniloc No ultrasonic cleaning	Inlet 5.5
2. Green River Kentucky Utilities	S. V. Anderson (502) 754-4541	Lime	Uniloc No ultrasonic cleaning	Inlet 8-8.5 Middle 7.5-8 Outlet 5.5-7
3. Cane Run No. 3 & 4 Louisville Gas and Electric	Mary Pederson (502) 566-4547	Carbide-Lime	Uniloc, Leeds and Northrop Ultrasonic cleaning	Inlet 8-8.5 Middle Outlet >6-7
4. Bruce Mansfield Pennsylvania Power Company	Tim Flora (412) 643-5000	Lime	Uniloc No ultrasonic cleaning	Discharge of scrubber and adsorber 7
5 Scholz Station Gulf Power (Southern Company Services)	Randall E. Rush (205) 870-6320	Dual Alkali Sodium/Calcium	Uniloc Leeds and Northrop (Ultrasonic cleaning on L&N in Reactor only)	Scrubber Effluent 5.0-6.5 Reactor Effluent 8.0-13.0
6. Sherburne County Northern States Power	Wayne Salo (612) 261-4100	Limestone	Uniloc Ultrasonic cleaning Electrofact (currently being tested	Outlet 4-6
7. Colstrip Montana Power	Carlton D. Grimm (406) 723-5421	Ash	Great Lakes No ultrasonic cleaning	Recycle 4.5-5.5 pump discharge
8. Lawrence #4. Kansas Power and Light Company	Kelly Green (913) 296-6300	Limestone	Uniloc ultrasonic cleaning	Outlet 5-7

(Continued)

TABLE 26. (Continued)

UTILITY	MAINTENANCE	TYPE OF PROBLEMS	HOW pH DATA IS EMPLOYED	AUTOMATED USE OF pH ELECTRODES
1. Shawnee, EPA/TVA Paducah, KY	3 times weekly acid wash	Scaling	Performance and control scaling	NO
2. Green River Kentucky Utilities	Once a week acid wash	No problems	Control scaling	Yes - Control of lime feed
3. Cane Run Louisville Gas and Electric	Once a week acid wash	Some type of scaling With L&N less scaling problem	General Operation Control Scaling	Yes - Control Lime feed
4. Bruce Mansfield Pennsylvania Power Company	3 times a week acid wash	No problems	Control or prevent scaling - optimize SO_2 scrubbing	Yes - control lime feed
5. Scholz Electric Gulf Power (Southern Company Services)	Once a week acid wash or when necessary, usually less frequently	Erosion of electrodes	Performance (not critical to operation)	No
6. Sherbourne County Northern States Power	Once a week or when necessary acid wash	Coating on electrodes (not gypsum)	Monitor chemical corrosion & erosion control relative additive feed	No
7. Colstrip Montana Power	Once a week acid wash	Erosion of electrodes	Prevent scaling	No
8. Lawrence #4. Kansas Power and Light Company	Less than once a week	Physical damage, scaling	Not used	Has automatic control capabilities but not used

TABLE 27. CHLORIDE ION MEASUREMENTS

Utilities	Chemistry	Do You Take Cl^- Ion Measurements*	Reasons for Sampling
1. Shawnee Test Facility EPA/TVA Paducah, Kentucky	Limestone	Yes	Effect on pH measurement and Cl^- for corrosion
2. Green River Power Station Kentucky Utilities	Lime	No	
3. Cane Run Louisville Gas and Electric	Carbine-Lime	No	
4. Bruce Mansfield Pennsylvania Power Co.	Lime	Yes-Grab samples	Cl^- for corrosion
5. Scholz Station Gulf Power (Southern Co., Services)	Dual-Alkali Sodium/ Calcium	Yes	Cl^- for corrosion
6. Sherburne County Northern States Power Becker, Minnesota	Limestone	No	
7. Colstrip Montana Power Co.	Ash	No	
8. Lawrence No. 4 Kansas Power and Light Co.	Limestone	No	

*The utilities which answered "No", in general, meant that their system was not affected by Cl^- to the extent that specific measurements had to be routinely performed.

Although the potential exists for chloride electrode application in automated control systems, the limited interest of surveyed companies in chloride measurements did not merit a pursuit of a chloride electrode evaluation test.

All companies surveyed measured pH with a standard non-self-cleaning pH electrode. The location of measurement points and the desired pH values varied considerably. Frequent acid washing of the electrode is necessary to remove the hard scale which forms around the electrodes. Even though ultrasonic cleaning shortens the electrode's life, three facilities have resorted to this technique for cleaning them.

The three lime scrubber sites, were the only sites that utilized the pH electrodes for an automated control system. This highlights the fact that lime has a much more consistent chemical composition than limestone. A system utilizing materials with consistent and predictable chemical compositions is much easier to automate than a system with chemically inconsistent materials. Thus, it is expected that automated lime scrubbing systems would be more prevalent than automated limestone systems.

It was found that accurate pH measurement of slurry streams is very important for proper operation and prevention of scaling, corrosion and erosion in an FGD unit. Paramount to successful pH electrode operation is the prevention of residue buildup and erosion of the electrode, clearly the most common problems among the utilities. The field evaluation test of a self cleaning and standard-type electrode was designed to solve these problems and to evaluate the applicability of the electrode in an automated system.

Evaluation of pH Electrode--

In this evaluation both the self-cleaning Electrofact 135G/Z electrode and a standard Uniloc pH electrode were tested. Both electrodes were placed in an external slurry pot fed from the venturi slurry stream at the Shawnee Test Facility. A separate line was fed into the control room so a grab sample could be taken and analyzed with a laboratory pH meter. Both meter chart recorder readings were obtained for the on-line electrodes.

Regular calibrations and measurements were obtained over a period of 576 hours; however, the two longest periods of continuous operation were only 214 and 140 hours.

Evaluation of the pH electrode test data revealed the following facts:

- The accuracy and precision of the self-cleaning and standard type electrode were nearly identical during the duration of the test.
- Scaling was a confirmed maintenance problem with the standard-type electrode.
- Clogging of the screen surrounding the electrode was a maintenance problem with the self-cleaning electrode used in slurry streams.
- The overall maintenance of both the self-cleaning and standard type pH electrode during continuous periods of operation less than two weeks were equal in slurry streams.
- For continuous periods of operation greater than two weeks in slurry streams, the self-cleaning electrode required slightly less maintenance.

2.25.4 Recommendations

The following recommendations are made for the application of chloride and pH electrodes to automated control systems in FGD units (slurry streams):

- Chloride measurements are not necessary unless FGD corrosion (high chloride values) is a problem or accurate pH calculations are required.
- For continuous periods of operation less than two weeks the use of either the standard type or self cleaning pH electrode is recommended.
- For continuous periods of operation greater than two weeks, the self-cleaning electrode is recommended and should require less maintenance.
- If the self-cleaning pH electrode is selected, the required maintenance should be significantly reduced when the wire screen surrounding the electrode is removed or the screen mesh size is increased.
- Additional comparisons at different FGD sites.
- Longer, uninterrupted periods of comparison.

SECTION 3

MINOR TASKS

3.1 TASK 11 MASS EMISSION MONITOR DEMO

This task was concerned with the selection of a site to demonstrate continuous flow measurement, gas sampling hardware and methodology. The future objective was to verify adequacy of hardware and procedures over a long time period. The NIPSCO facility in Gary, Indiana, was selected as the site for the demonstration of the above activities. The effort initiated in this task was completed under Task 49.

3.2 TASK 16 MBS MEETING

Under this task a representative of TRW attended the symposia on "Methods and Standards for Environmental Measurement." Papers were presented in the following areas:

- Single and multielement technique development
- Physical and chemical characterizations of aerosols
- Organometallic sampling and analysis
- Laser sensing methods
- Environmental standards.

Table 28 lists the individuals who presented papers and the subject area.

TABLE 28. CURRENT RESEARCH IN MEASUREMENTS OF INORGANIC SPECIES

Name	Address	Current Research	Potential Areas of TLE Interest
Peter Pella	NBS Analytical Chemistry Division Washington, DC 20234	The use of this film and borate fusion powders are being studied for use as XRF standards.	The generation of known particles and collection on glassfiber filters as a means of preparing XRF standards for high volume stack or ambient samplers.
Edward Murray	Stanford Research Institute 333 Ravenwood Ave. Menlo Park, Ca. 94035	Using differential absorption with NO_2, SO_2, O_3, H_2O, $HC\ell$, H_2O, and CH_y were monitored.	The use of lasers to monitor concentractions of $HC\ell$ and SO_3 (H_2SO_4).
Mohammad Fatemi	NRL 4555 Overlook Avenue Washington, DC 20375	Identification and quantification of asbestos fibers using electrostatic alignment prior to XRD analysis.	Sensitivity of XRD for environmental compounds as well as means of sample preparation and standard generation.
R.T. Ku	MIT Lincoln Labs 244 Wood Street Lexington, Ma. 02173	Solid State lasers (PbSnTi) used to measure CO over 1 kw	The use of lasers to monitor in stack circumstances of $HC\ell$ and SO_3 (H_2SO_4).
Peter Lott	U. of Missouri Chemistry Dept. Kansas City, Mo.	Particulate matter from Pb smelters was identified using XRD	Extending and quantifying XRD analysis of environmental samples to Hg, As, and Cd compounds.

(Continued)

TABLE 28. (Continued)

Name	Address	Current Research	Potential Areas of TLE Interest
Robert Bramer	U. of S. Florida Dept. of Chemistry Tampa, Florida	Using selective solid supports to sample organomercury, arsenic and selenium compounds.	Using the solid supports for sampling flue gas streams.
Eris Crecelius	Bettelle Richland, Wa 99352	Studied as compounds found in human urine samples.	Discuss the use of this modification to Bramer's techniques applied to process water streams.
Ronald Hurley Eugene White	Materials Research Lab Penn State U. University Park, PA 16802	Sulfur forms in coal using XRF	Application of XRF analysis of sulfur forms to environmental samples
Donald Reamer	U. of Maryland Dept. of Chemistry College Park, Md.	Sampling organometallic compounds with solid absorbants followed by GC/microwave detection.	Interferences to his collection system, especially SO_2 and H_2S
John Gilfrich	NRL Code 6481 Washington, DC	Sulfur valince state using a wavelength dispersive XRF.	Application of wavelength dispersive XRF to differentiate between other elements and their anions.
Mortega Janghorbani	Environmental Trace Substances Research Center Columbia, Mo.	Extraction of trace elements in aqueous medis.	Discuss the possible GC quantification and identification of metal ion chelates, as well as current research at ETSRC.

(Continued)

TABLE 28, (Continued)

Name	Address	Current Research	Potential Areas of TLE Interest
Lee Hanson	Thermochemical Institute Brigham Young U. Provo, Utah 84602	Thermometric titration of sulfur compounds in environmental samples	Application of this approach to complex samples such as those attained from process gas streams.
John Small	NBS Analytical Chemistry Division Washington, DC	SEM-EDX of individual particles	Sensitivity for compound analysis and potential of SEM selective area diffraction for compound analyses.
R. Stafford	Dept. of Engineering & Applied Science Yale U. Becton Center New Haven, Conn. 06520	Laser Raman of suspended ambient sulfate particles.	Application of this approach to real time identification of stack effluent particles.
E.S. Etz	NBS Analytical Chemistry Division Washington, DC 20234	Laser Raman of individual particles collected on membrane filter.	Application of this approach to material collected in the cyclones on filters of a SASS train.
Douglas Segar	NOAA Code C61 Rockville, MD 20852	Liquid chromatography separation of organometallic compounds followed by flameless AAS	Extension of this technique to complex wast streams.
David Burrell	Institute of Marine Science U. of Alaska Fairbanks, Alaska 99701	Reverse voltametric analysis of complex ions in saline waters	Application to process streams where organic might be present.

(Continued)

TABLE 28. (Continued)

Name	Address	Current Research	Potential Areas of TLE Interest
Richard Dinst	NBS Analytical Chemistry Divison Washington, D.C.	Anodic stripping voltametry to determine cadmium speciation in natural waters.	Extension of ASV to process stream waters.
Cary Gravatt	NBS Analytical Chemistry Division Washington, D.C.	Differential light scattering of polarized light	Development of a liquid aerosol counter capable of discrimination between dry and liquid aerosols in the same stream.

3.3 TASK 28 SASS - SO_2 TESTS

The objective of this task was to determine if the SASS train condensation module can be used to collect H_2SO_4 while avoiding a large positive error due to SO_2 oxidation in either gas or liquid phases. The results of this task were:

- SO_2 ($SO_3^=$) oxidation to SO_3 ($SO_4^=$) ranges from 0.05-0.9 percent.
- The above range makes a prediction of the expected background level of $SO_4^=$ difficult.

The following recommendations were made as a result of this task:

- Further tests should be run to measure the SO_2 oxidation rate to develop a statistical base for predicting the potential SO_2 interference.
- Evaluations should be made of the effect of storage and analysis procedures on the $SO_3^=/SO_4^=$ ratio.

3.4 TASK 29 SO_3 MEASUREMENT PRESENTATION

The objective of this task was to present to IERL contractors the methodology developed by TRW to measure H_2SO_4 in particle laden flue gas streams. On February 22, 1977 the proposed quality assurance program for the H_2SO_4 measurements at the Shawnee FCD Test Facility was reviewed by Bob Statnick (IERL) and Frank Smith (RTI). On February 23, 1977, TRW gave two presentations on the H_2SO_4 measurement methodology concerning:

1. The use of the controlled condensation procedure in the field.
2. The presentation of the laboratory data from Task 13.

3.5 TASK 33 DENVER X-RAY MEETING

Under this task TRW representative attended the Denver Symposium on "Applications of X-Ray to Environmental and Occupational Health Analyses". The Symposium was sponsored by the Denver Research Institute, University of Denver and Phillips Electronic Instruments. Papers were presented on the following instrumental methods of analysis:

- X-Ray Diffraction
- Electron Microprobe
- Electron Microscopy

Table 29 lists the individuals who presented papers and the subject area.

TABLE 29. CURRENT RESEARCH IN APPLICATIONS OF X-RAY TO ENVIRONMENTAL AND OCCUPATIONAL HEALTH ANALYSES

Name	Address	Current Research
J. Crouse	Colorado School of Mine	XRD analysis of asbestos impurities found in talc
Phillip Cook	Environmental Research Laboratory	XRD to monitor asbestos in air
George Wadler	Amoco Steel	XRD analysis of various silicon phases
Kurt Heinrich	NBS	Electron microprobe analysis as a qualitative technique
John Armstrong	University of Arizona	Electron microprobe techniques for determination of fly ash composition
Ed Peters	ADL	Transmission electron microscopy analysis on asbestos
Ian Steward	McCrane Associates	Asbestos in various tissues
Phil Russel	Denver Research Institute	TEM and SEM analysis of smog
Bernard Harris	Battelle Columbus Laboratory	X-ray fluorescence techniques for total sulfur in natural and trented coal.

3.6 TASK 44 PARTICULATE MEASUREMENT MEETING

Under this task a TRW representative attended the "Symposium on High Temperature, High Pressure Particulate Control". The Symposium was sponsored by EPA/DOE and was held in Washington D.C. on September 20 and 21, 1977. TRW's past experience most closely relates to the presentations given in Session IV: Particle Sampling and Measurement. TRW has built an extractive particle/slag sampling system for use in a high pressure coal combustor, and informal exchanges of information took place with Aerotherm engineers who have been working in the same area. With regard to particulate control technology, it was made clear that while there are various proposed techniques, none are yet fully proven and operational.

3.7 TASK 45 SASS TRAIN THERMAL CONTROL ALTERNATE

The objective of this task was to determine an alternate thermal control system for the Source Assessment Sampling System (SASS) presently being manufactured by Aerotherm Corporation, Mountain View, California. This sampling system is utilized in EPA Level 1 Environmental Assessment. The results of this task were:

- A thermodynamic analysis of the thermal control system was performed to determine the requirement of the system under normal and/or extreme operating conditions.
- The optimum system for the alternative design was composed of two immersion coolers which would be used with the existing cooling bath.
- Total cost for the modification to the system would be $1040.

3.8 TASK 46 STEPWISE ARSENIC PROCESS

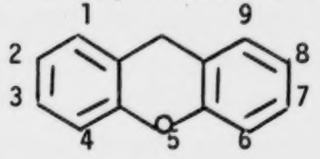
The objective of this task was to evaluate a proposed Level 1 arsenic procedure based on atomic absorption spectrometry in terms of its accuracy, precision, percentage recovery, efficiency of usage. The results of the evaluation were:

1. For quantification, measuring the area under the absorbance peak is more reliable than measuring peak height.
2. Sodium borohydrate reduces arsenic to arsine more effectively than stannous chloride — zinc slurry (25% better response).
3. Stepwise arsenic procedure had a precision of less than 5% (Level 1).
4. A relative error of 11 percent was obtained when analyzing a NBS coal fly ash standard.
5. Greater than 85% of the arsenic added to each Level 1 sample matrix was recovered.

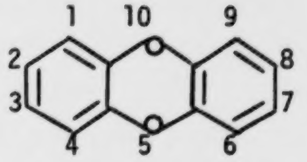
3.9 TASK 54 FATE OF PCB's IN ROLLINS ENVIRONMENTAL SERVICES PLANT FIRE

The objective of this study was to investigate the fate of polychlorinated biphenyl compounds (PCB's) that were stored in a tank farm at a chemical disposal site when a catastrophic fire struck the facility in December 1977. The PCB's were selected for study because they are not only toxic and environmentally long lived, but they may also serve as precursors for the formation of new compounds which are even more toxic. This study attempts to define what new products may have been formed under the conditions that existed at the time of the accident.

Two compounds of particular concern that may have been formed are the polychlorinated dibenzofurans and the polychlorinated dibenzo-p-dioxins. Both of these compounds are highly toxic when partially chlorinated. Dioxins have been shown to have pronounced fetotoxic and some teratogenic effects even in the absence of any noticeable acute toxicity.



Dibenzofuran



Dibenzo-p-dioxin

The formation of polycyclic aromatic hydrocarbons (PAH's) from PCB's also is a concern because they are known carcinogens. PAH formation is favorable under pyrolysis (no oxidizing species present) and oxygen deficient conditions which were expected to have existed as a result of the fire.

The study was divided into three major elements of activity. The first activity was dedicated to the definition of the probable conditions to which the PCB's were exposed. The second activity addressed the question of what new products could be formed given the conditions that were defined in the first activity. The approach employed to define the new products was to allow the PCB's to react with the simple radical species likely to exist in combustion processes. Particular emphasis was placed on the formation of dibenzofurans and dibenzo-p-dioxins. Part of this activity was also directed to a definition of how the PCB's and reaction products may have been dispersed in the environment during the accident. The last activity summarized results of commercial scale incineration of PCB materials for comparison to the results of this study.

This study concluded that under certain conditions polychlorinated biphenyl compounds may serve as precursors for the formation of other environmentally undesirable compounds. The most probable class of compounds formed are dibenzofurans. The reaction pathways to these compounds seemed to be favorable under oxygen deficient combustions and low temperature. Conversely, it seems improbable that dibenzo-p-dioxins are formed under similar conditions. If dibenzo-p-dioxins were to be formed, they would come from the dibenzofurans that are initially generated from the PCB's. Formation of polycyclic aromatic hydrocarbons (PAH) is possible via pyrolysis of PCB's. in oxygen deficient conditions that could have existed in the Rollins fire.

3.10 TASK 58 WORKSHOP PRESENTATION

The Environmental Sciences Research Laboratory, EPA/RTP, sponsored a workshop on Measurement Technology and Characterization of Primary Sulfur Oxides Emission from Combustion Sources in North Carolina during April 1978. The objectives were 1) to review and discuss current measurement methods and problem areas for sulfur oxide emissions with attention focused on sulfuric acid, sulfates and sulfur-bearing particulate matter; 2) to review and discuss emission data based on application of these methods to various combustion sources under different operating conditions; and 3) to delineate and recommend areas in need of further research and development. Dr. R. F. Maddalone presented a paper, "Sulfur Emissions Sampling and Analysis," detailing work techniques for sampling and analyzing SO_2, H_2SO_4 and particulate sulfate emissions from flue gas desulfurization units.

SECTION 4

REPORTS ISSUED

Task 1.

Hamersma, J. W., S. L. Reynolds, and R. F. Maddalone. IERL-RTP Procedures Manual: Level 1 Environmental Assessment. EPA-600/2-76-160a, June, 1976.

Task 2.

Maddalone R. F., A. Grant, D. Luciani, and C. Zee. Procedures for Aerosol Sizing and SO_3 Vapor Measurements at TVA Shawnee Test Facility. EPA-600/7-79-152, July, 1979.

Task 5.

Zee, C. A., D. G. Ackerman, J. F. Clausen, M. L. Kraft, and S. L. Reynolds. Draft Report. Evaluation of the SASS Train and Level 1 Sampling and Analysis Procedures Manual. Prepared for U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1976.

Task 7.

Maddalone, R. F., L. E. Ryan, R. Delumyea, and M. M. Yamada. Technical Manual for Level 2 Inorganic Compound Analysis. EPA 600/2-79-200, November, 1979.

Task 8.

Beimer, R. G., H. E. Green, and J. R. Denson. EPA/IERL-RTP Procedures Manual: Level 2, Sampling and Analysis of Selected Reduced Inorganic Compounds. EPA-600/2-79-199, November, 1979.

Task 9.

Brooks, E. F., and C. W. Clendening. Assessment of Instrumentation for Monitoring Coal Flow rate and Composition. EPA-600/7-79-196, August, 1979.

Task 10.

Hamersma, J. W., and M. L. Kraft. Coal Sulfur Measurements. EPA-600/7-79-150, July, 1979.

Task 12.

Brooks, E. F., N. Gat, M. E. Taylor, T. E. Chamberlain, R. J. Golik, and R. Watson. Development Study of a Novel Continuous-Flow Impactor, EPA-600/7-80-014, January, 1980.

Task 13.

Maddalone, R. F. and N. Garner. Process Measurement Procedures: H_2SO_4 Emissions. EPA-600/7-79-156, July, 1979.

Task 14.

Reynolds, S. L., D. G. Ackerman, J. F. Clausen, M. L. Kraft, and C. A. Zee. Draft Report, SASS Train and Level 1 Procedures Evaluation. Prepared for the U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1976.

Task 22.

Lutz, S. J., R. C. Christman, B. C. McCoy, S. W. Mulligan, and K. M. Slimak. Evaluation of Dry Sorbents and Fabric Filtration for FGD. EPA-600/7-79-005, January, 1979.

Task 26.

Brooks, E. F.. Total Particulate Mass Emission Sampling Errors. EPA-600/7-79-155, July, 1979.

Task 32.

Kraft, M. L., and L. E. Ryan, Letter Reports:

1. "Problems and Deficiencies/Level 1 Environmental Assessment Procedures," April 15, 1977
2. "Parr Bomb Combustion Procedures," May 6, 1977.
3. "Step-Wise Antimony, Mercury and Arsenic Procedures," June 3, 1977.
4. "Effecting the Recovery of As and Hg from Level 1 Impinger Solutions," July, 1977.

Task 36.

Reynolds, S. L., and L. E. Ryan, Draft Report. Inorganic MEG Compounds and Level 1 Assessment Detection Capability. Prepared for U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1977.

Task 45.

Knight, B. A. Alternative SASS Train Thermal Control System. Prepared for U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1977.

Task 46.

Yu, C. L., Draft Report. Atomic Absorption Analysis of Arsenic for Level 1. Prepared for U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1978.

Task 47.

Knight, B. A., E. F. Brooks, and R. F. Maddalone. Development of an Automatic Sulfur Trioxide Monitor. EPA-600/7-79-153, July, 1979.

Task 48.

Acciani, T. R., and R. F. Maddalone. Chemical Analysis of Wet Scrubbers Utilizing Ion Chromatography. Prepared for U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1978.

Task 49.

Brooks, E. F. Field Demonstration of High Accuracy Continuous Flow and Gas Composition Methodology (Draft) prepared for EPA under Contract 68-02-2165, RTP, July, 1979.

Task 51.

Acciani, T. R. and R. F. Maddalone. Particle Sizing and Trace Elements Analysis Approaches. Prepared for U. S. Environmental Portection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1978.

Task 53.

Zee, C. A.; Hamersma, J. W.; Maddalone, R. F.; Ung, C. Y.; TRW Input to Level 1 Manual Revisions - Chapters II, III, and VII. Prepared for U.S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1978.

Task 54.

O'Rell, M. K. Fate of PCB's in Rollins Environmental Services Plant Fire. Prepared for U. S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1978.

Task 57.

Fisher, H. J. At-Sea Incineration of Organochlorine Wastes: Environmental Aspects and Impacts of Adopting International Regulatory Standards, Prepared for U.S. Environmental Protection Agency under Contract No. 68-02-2165, Research Triangle Park, No. Carolina, 1978.

Task 62.

Ung, C. Y., T. R. Acciani and R. F. Maddalone. pH and Chloride Sensitive Electrodes. EPA 600/2-79-202, November, 1979.

SECTION 5

REFERENCES

1. "Status of Ocean Incineration of Organic Chlorides Aboard Matthias III as of 29 June 1976," TRW Report, EPA Contract 68-01-2966.

2. "Status of Ocean Incineration of Organic Chloride Aboard Matthias III as of 3 September 1976," dated November 12, 1976, EPA Contract 68-02-2165.

3. "At-Sea Incineration of Organochlorine Wastes Onboard the M/T Vulcanus," dated September 1977, EPA-600/2-77-196.

4. "Rationale for Annex A to Suggested Special Provisions for Control of Incineration at Sea," dated 18 February 1977, TRW Report on EPA Contract 68-02-2165.

5. Bramen, R. S., Justin, L. L. and Forebeck, C. C., "Direct Volatilization-Spectral Emission Type Detector System for Nanogram Amounts of As and Sb", *Anal. Chem.*, *44*, 2195 (1972).

6. Estep, P. A., Kovach, J. J., Waldstien, P. and Karr, C., "Infrared and Raman Spectroscopic Studies of Structural Variations in Minerals from Apollo 11, 12, 14, and 15 Samples," *Geochimica Et Cosmochimica Acta*, *3*, 3047 (1972).

7. Lunsford, J. H., "Structure and Reactivity of Absorbed Oxides of Sulfur," Dept. of Chemistry Texas A&M, PB-245-046, August 1974.

8. Miller, F. A. and Wilkins, C.H., "Infrared Spectra and Characteristic Frequencies of Inorganic Ions," *Anal. Chem.*, *24* (8), 1253 (1252).

9. Miller, F. A. and Wilkins, C. H., Bentley, F. F. and Jones, W. H., "Infrared Spectra of Inorganic Ions in the Cesium Bromide Region (700-300cm^{-1})," *Spectrochimica Acta*, *16*, 135-235 (1960).

10. Kolthoff, I. M., Laitinen, H. A. and Lingane, J. J., *J. Am. Chem. Soc.*, *59*, 429 (1937).

11. Bramen, R. S., and Johnson, D. L., "Selective Absorption Tubes and Emission Technique for Determination of Ambient Forms of Mercury in Air," *Environ. Sci. Technol.*, 8, 996 (1974).

12. B.P. Knol, "Improvements in Determination of SO$_3$ and SO$_2$ in Combustion Gases", *Riv. Combustible*, 4, 542 (1960).

13. H. Goksoyr and K. Ross, "The Determination of Sulfuric Trioxide in Flue Gases", *J. Inst. Fuel*, 35, 177 (1962).

14. American Society of Testing Materials, Part 26, ASTM Method D3226-73T, 1974.

15. E. S. Lisle and J. D. Sensenbaugh, "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases", Combustion, **36**, 12 (1965).

16. J. N. Driscol and A. W. Berger, "Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from Combustion of Fossil Fuels. Volume I, Sulfur Oxides", Walden Research Corporation, PB 209-267, June, 1971.